Acta Cryst. (1992). C**48**, 1–4

The Importance of Accurate Crystal Structure Determination of Uranium Minerals. II. Soddyite $(UO_2)_2(SiO_4).2H_2O$*

By Francesco Demartin

Istituto di Chimica Strutturistica Inorganica, Università degli Studi, Via Venezian 21, *I*-20133 *Milano, Italy*

Carlo M. Gramaccioli

Dipartimento di Scienze della Terra, Università degli Studi, Via Botticelli 23, *I*-20133 *Milano, Italy*

and Tullio Pilati

Centro CNR per lo Studio delle Relazioni fra Struttura e Reattività Chimica, Via Golgi 19, *I*-20133 *Milano, Italy*

(*Received* 3 *February* 1991; *accepted* 1 *May* 1991)

Abstract. $(UO_2)_2(SiO_4).2H_2O$, $M_r = 668.17$, orthorhombic, *Fddd*, $a = 8.334\,(2)$, $b = 11.212\,(5)$, $c = 18.668\,(6)$ Å, $V = 1744\,(1)$ Å^3, $Z = 8$, $D_x = 5.088$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 353.38$ cm^{-1}, $F(000) = 2256$, $T = 293$ K, $R = 0.014$, $wR = 0.018$ for 335 independent reflections with $I > 3\sigma(I)$. A least-squares refinement of the structure of soddyite from a new set of X-ray data shows that accurate results can be obtained even for crystals containing very heavy elements; the strong absorption can be satisfactorily accounted for if appropriate procedures are used. Here, in particular, it was even possible to locate the water H atoms and refine their coordinates and thermal parameters. The structure shows chains of pentagonal bipyramids centred on the U atoms, joined by edge sharing: the chains are parallel to [110] and are cross linked through SiO_4 tetrahedra. The cohesion within the resulting three-dimensional structure is further enhanced by a pattern of hydrogen bonds involving the water molecules and the uranyl O atoms.

Introduction. An example of the importance of using accurate diffraction data and careful refinement in establishing the chemical composition of uranium compounds has already been reported by us (Demartin *et al.*, 1991): here the results are considerably different from similar works on the same substance, including the presence of additional components (see, for comparison, Piret & Piret-Meunier, 1991). Pursuing our interest in this problem, we have redetermined the structure of the uranium mineral soddyite $(UO_2)_2(SiO_4).2H_2O$.

A partial model of the crystal structure of soddyite was originally proposed by Stohl (1974) (see also Stohl & Smith, 1974) on the basis of the similarity of unit-cell parameters, space group, and X-ray powder patterns between natural soddyite and the synthetic hydrated uranyl silicate and uranyl germanate studied by Legros, Legros & Masdupuy (1972). A refined model of the uranyl germanate structure was subsequently reported by Legros & Jeannin (1975) and essentially supported these previous data; this model was also confirmed by a structure analysis carried out on a synthetic soddyite crystal by Belokoneva, Mokeeva, Kuznetsov, Simonov, Makarov & Belov, (1979). The refinement carried out by these authors led to a final value of 0.064 for the *R* index, which indicates the main features to be essentially correct; however, for some atoms implausible values for thermal parameters were obtained, very probably because of the lack of adequate absorption correction. For this reason, and as no structure determination on the naturally occurring mineral has been reported so far, we thought a reinvestigation of this structure on a natural sample to be advisable.

Experimental. Natural soddyite usually occurs as amber–yellow zoned crystals, with bipyramidal habit; they are usually opaque at the centre and transparent near the surface. The sample used in this work is from an unstated locality in Zaire, probably Swambo. A splinter having an irregular shape and measuring 0.05 × 0.12 × 0.21 mm was obtained from a transparent zone of a crystal and mounted on an Enraf–Nonius CAD-4 diffractometer. 25 intense reflections having a 2θ value in the range 19.4–31.3° were centred using graphite-monochromated Mo $K\alpha$ radiation: from least-squares refinement of their set-

---

* Part I: Demartin, Diella, Donzelli, Gramaccioli & Pilati (1991).

0108-2701/92/010001-04$03.00

ting angles the unit-cell parameters were deduced, together with an orientation matrix relating the crystal axes to the diffractometer axes. A total of 827 diffracted intensities [636 with $I > 3\sigma(I)$, 335 unique] were collected at room temperature with variable ω-scan speed determined from pre-scans, requiring $I > 0.5\sigma(I)$ [maximum scan time for each reflection 120 s, ω-scan width $(1.9 + 0.35\tan\theta)$°], by exploring the quadrant of the reciprocal lattice with $-11 \leq h \leq 11$, $0 \leq k \leq 15$ and $0 \leq l \leq 26$, out to a maximum 2θ angle of 50°. The diffracted intensities were corrected for Lorentz, polarization and background effects. Three different absorption correction procedures were tested and the results are shown in Table 1. In this table column (1) shows the results of an empirical absorption correction applied according to North, Phillips & Mathews (1968), using a set of ψ scans for six reflections having a χ value close to 90°. In column (2) the corresponding results are reported after a *DIFABS* absorption correction (Walker & Stuart, 1983). The third column (3) reports the results of a ψ-scan absorption correction followed by a *DIFABS* correction. For comparison, the corresponding results obtained without the absorption correction are also given [column (4)]. All the absorption correction procedures adopted here are satisfactory on the basis of the improvement of the agreement index between equivalent reflections, of the reasonable values obtained for thermal parameters (see Table 2), of the lower values of the final R and wR indices and of the maximum residual electron density peaks; these highest peaks are observed, in the present case, close to the U atom. In the absence of absorption correction the refinement yielded a non-positive-definite thermal parameter for Si and it was impossible to locate the H atom of the water molecule. The best results derive from procedures (2) and (3), in which the absorption correction is θ dependent. In any case, whatever correction is applied, the improved accuracy of data provides clearer details regarding the lighter atoms. The structural parameters discussed hereafter refer to the data corrected using the procedure (3).

Scattering factors for neutral atoms and anomalous-dispersion corrections for scattering factors were taken from Cromer & Waber (1974) and Cromer (1974) respectively. Starting from the atomic positions reported by Belokoneva *et al.* (1979), the structure was refined by full-matrix least squares (on F), minimizing the function $\sum w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{\frac{1}{2}}/2F_o\mathrm{Lp}$, $\sigma^2(I)$ is the standard deviation for each reflection as derived from counting statistics, k (= 0.03) is a coefficient for improving the goodness of fit and Lp is the Lorentz–polarization factor. Anisotropic thermal parameters were assigned to all the atoms with the exception of the water H atom, which was located in a final difference Fourier map and refined isotropically. Final $R = 0.014$, $wR = 0.018$; $(\Delta/\sigma)_{\max} = 0.01$, for 36 variables. All the calculations were performed on a PDP11/73 computer using the *SDP-Plus Structure Determination Package* (B. A. Frenz & Associates, Inc., 1980).

Table 1. *Comparison of the results obtained from different absorption corrections*

	(1)	(2)	(3)	(4)
Agreement factor (on F_o) between equivalent observed reflections	0.029	0.015	0.013	0.034
R and wR indices	0.025, 0.031	0.016, 0.021	0.014, 0.018	0.048, 0.057
Maximum residual electron density peak (e Å^{-3})	2.3 (2)	1.4 (1)	1.1 (1)	4.2 (6)
Range of transmission factors	0.45–1.00	0.79–1.25	0.85–1.16	–

(1) Performed using the ψ-scan method according to North *et al.*, (1968). (2) Performed by *DIFABS* according to Walker & Stuart (1983). (3) Performed by a ψ-scan correction followed by *DIFABS*. (4) No absorption correction performed.

Table 2. *Final atomic fractional coordinates and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

The H atom was refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as $B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	Multiplicity	x	y	z	$B_{\rm eq}$
U	0.50	0.3750	0.3750	0.04413 (1)	0.814 (6)
Si	0.25	0.1250	0.1250	0.1250	0.86 (5)
O(1)	1.00	0.5522 (6)	0.2862 (5)	0.0454 (2)	1.47 (9)
O(2)	1.00	0.2243 (6)	0.2063 (4)	0.0677 (2)	1.27 (8)
O(*W*)	0.50	0.3750	0.3750	0.1730 (4)	2.3 (1)
H	1.00	0.30 (1)	0.394 (9)	0.193 (4)	4 (2)

The final atomic coordinates and thermal parameters with their e.s.d.'s are listed in Table 2.*

Discussion. Projections of the soddyite structure along the a and c axes of the unit cell are given in Figs. 1 and 2, respectively. Selected interatomic distances and angles are reported in Table 3. The U atoms in the present structure display a pentagonal bipyramidal coordination; the two O atoms of the uranyl group UO_2^{2+} [O(1) and its symmetry related companion] are in the apical position at 1.781 (5) Å from the metal, and the remaining five [four O(2) plus O(*W*)] lie in the equatorial plane. The equatorial U—O distances range from 2.313 (4) to 2.424 (4) Å. In these coordination polyhedra, the distances between adjacent O atoms range from 2.462 (9) to 3.126 (7) Å, the shortest values corresponding to shared edges with other U-centred bipyramids or with SiO_4 groups.

---

* Lists of anisotropic temperature factor coefficients and observed and calculated structure factor moduli have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54162 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The pentagonal bipyramids centred on U are connected together by sharing two non-adjacent edges of the equatorial plane to form zigzag chains (see Fig. 1), and the water molecules are alternated in opposite directions. These chains are parallel to [110] (see Fig. 2), and are cross bonded through two opposite edges of the SiO_4 tetrahedra. Moreover, the cohesion between parallel chains is enhanced by a pattern of hydrogen bonds involving the water molecules and the uranyl O atoms. The SiO_4 tetrahedron is markedly irregular, the O—Si—O angles ranging from 98.0 to 119.0°, and the O···O contacts ranging from 2.462 (9) to 2.811 (9) Å. The Si—O distances [1.631 (4) Å] are within the normal range. These features are essentially in agreement with similar observations made by Stohl & Smith (1981) for some uranyl silicate minerals. The geometry and the orientation of the plane of the water molecule are reasonable; the latter is determined by a hydrogen-bond interaction, directed towards O(1) (see Fig. 2).

In conclusion, another example of an accurate structure determination performed on a uranium mineral is given here. The results clearly show that, if good data are collected from a suitable crystal and provided that appropriate correction for the high absorption is made, some details regarding even the lightest atoms (in the present case the location and refinement of the water H atoms) can be evident. For this purpose empirical routines can be particularly useful, especially when the crystal has an irregular shape which renders application of numerical integration difficult. In our opinion, the best absorption correction procedure should be chosen *a posteriori* according to comparative tests between the various results. This is also advisable because the advantages of the different routines with respect to each other depend not only on the absorption coefficient and the size of the crystal, but also on the particular shape of the sample selected.

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *in soddyite with e.s.d.'s in parentheses*

Tetrahedron around Si			
Si—O(2)	1.631 (4)		
O(2)···O(2)^a × 2	2.811 (9)	O(2)—Si—O(2)^a × 2	119.0 (3)
O(2)···O(2)^b × 2	2.705 (9)	O(2)—Si—O(2)^b × 2	112.0 (3)
O(2)···O(2)^c × 2	2.462 (9)	O(2)—Si—O(2)^c × 2	98.0 (3)
Pentagonal bipyramid around U			
U—O(1) × 2	1.781 (5)	U—O(2) × 2	2.313 (4)
U—O(2)^d × 2	2.424 (4)	U—O(*W*)	2.406 (8)
O(1)···O(2)^d × 2	3.126 (7)	O(1)—U—O(2)^d × 2	94.8 (2)
O(1)···O(2)^e × 2	2.925 (7)	O(1)—U—O(2)^e × 2	90.3 (2)
O(1)···O(2)^f × 2	2.918 (6)	O(1)—U—O(2)^f × 2	86.5 (2)
O(1)···O(2) × 2	2.906 (7)	O(1)—U—O(2) × 2	89.5 (2)
O(1)···O(*W*) × 2	2.974 (8)	O(1)—U—O(*W*) × 2	89.2 (1)
O(2)···O(2)^d × 2	2.745 (9)	O(2)—U—O(2)^d × 2	70.8 (2)
O(2)^d···O(2)^f	2.462 (9)*	O(2)^d—U—O(2)^f	61.1 (2)
O(2)···O(*W*) × 2	3.003 (7)	O(2)—U—O(*W*) × 2	79.0 (1)
		O(1)—U—O(1)^c	178.5 (3)
Water molecule			
O(*W*)—H	0.76 (10)	H—O(*W*)—H^c	121 (15)
H···O(1)^g	2.22 (10)	O(*W*)—H···O(1)^g	156 (10)

Symmetry code: (*a*) $x, \frac{1}{4}-y, \frac{1}{4}-z$; (*b*) $\frac{1}{4}-x, y, \frac{1}{4}-z$; (*c*) $\frac{1}{4}-x, \frac{1}{4}-y, z$; (*d*) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (*e*) $\frac{3}{4}-x, \frac{3}{4}-y, z$; (*f*) $\frac{1}{4}+x, \frac{1}{4}+y, -z$; (*g*) $-\frac{1}{2}+x, \frac{3}{4}-y, \frac{1}{4}-z$.

* Edge shared with the tetrahedron centred on Si

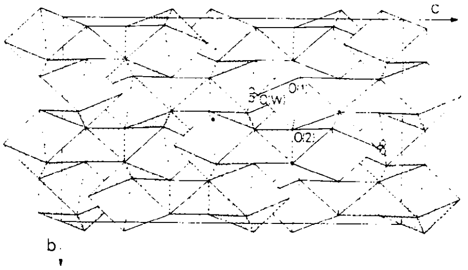

Fig. 1. Projection of the soddyite structure along the *a* axis of the unit cell, obtained by program *POLIEDRI* (Pilati, 1990). A chain of pentagonal bipyramids centred on the U atoms is evidenced by erasing the shading. The H atoms of the water molecules of this chain, whose O atom is O(*W*), are represented by open circles; the tetrahedra centred on Si atoms are also evident.

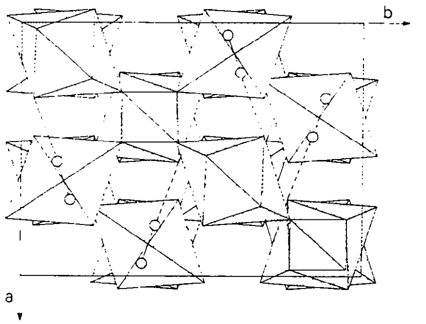

Fig. 2. Projection along the *c* axis of the unit cell, obtained by program *POLIEDRI* (Pilati, 1990). Dashed lines represent the hydrogen bonds between O(1) and water molecules.

Note added in proof. When our paper was in the press, a refinement of the structure of soddyite, performed using data from neutron diffraction on a powdered synthetic specimen, appeared in the literature [Nozik & Kuznetsov (1990). *Kristallografiya*, **35**, 1563–1564]. With respect to the results of Belokoneva *et al.* (1979), this work shows a better agreement with experimental data ($R = 0.021$, $wR = 0.029$), but no location of the H atom is reported.

References

B. A. Frenz & Associates, Inc. (1980). *SDP-Plus*. Version 1.0. Enraf–Nonius, Delft, The Netherlands.

Belokoneva, E. L., Mokeeva, V. I., Kuznetsov, L. M., Simonov, M. A., Makarov, E. S. & Belov, N. V. (1979). *Dokl. Akad. Nauk SSSR*, **246**, 93–96.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

DEMARTIN, F., DIELLA, V., DONZELLI, S., GRAMACCIOLI, C. M. & PILATI, T. (1991). *Acta Cryst.* **B47**, 439–446.

LEGROS, J. P. & JEANNIN, Y. (1975). *Acta Cryst.* **B31**, 1140–1143.

LEGROS, J. P., LEGROS, R. & MASDUPUY, E. (1972). *Bull. Soc. Chim. Fr.* **8**, 3051–3060.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

PILATI, T. (1990). *Acta Cryst.* **A46**, C-69.

PIRET, P. & PIRET-MEUNIER, J. (1991). *Eur. J. Mineral*, **3**, 69–77.

STOHL, F. V. (1974). PhD Thesis, Pennsylvania State University, University Park, USA.

STOHL, F. V. & SMITH, D. K. (1974). *Am. Crystallogr. Assoc. Meet. Program Abstr. Ser.* 2, **2**, 271.

STOHL, F. V. & SMITH, D. K. (1981). *Am. Mineral.* **66**, 610–625.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1992). **C48**, 4–5

Structure of Tricaesium Diaquanonaazidedineodymate(III)

BY P. STARYNOWICZ

Institute of Chemistry, University, 14 F. Joliot-Curie Str., 50383 Wroclaw, Poland

(*Received* 19 *March* 1991; *accepted* 9 *July* 1991)

Abstract. $Cs_3[(H_2O)_2(N_3)_9Nd_2]$, $M_r = 1101.4$, triclinic, $P\bar{1}$, $a = 6.791\ (5)$, $b = 9.107\ (6)$, $c = 10.683\ (7)$ Å, $\alpha = 99.84\ (5)$, $\beta = 99.19\ (6)$, $\gamma = 110.56\ (6)°$, $V = 592.0\ (9)$ Å^3, $Z = 1$, $D_m = 3.08$, $D_x = 3.089\ (4)$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 9.03$ mm^{-1}, $F(000) = 494$, $T = 302\ (1)$ K, final $R = 0.047$ for 1894 reflections. The Nd cations are eight coordinate (seven N atoms and a water molecule) and together with azide anions form a two-dimensional complex polymer network.

Introduction. Spectroscopic investigation of anhydrous complex caesium neodymium azides (Gatterer, Day, Fritzer & Sperka, 1988) indicated ninefold coordination of the Nd cation. Since, to the author's knowledge, no X-ray structure analysis of these systems has been reported, it was thought that it would be interesting to investigate the title complex which contains lanthanide–nitrogen bonds.

Experimental. The title compound was prepared by placing vessels containing an aqueous suspension of freshly precipitated $Nd(OH)_3$ with some Cs_2CO_3 added, together with a source of HN_3 ($NaN_3 + HClO_4$ in water), and a drying agent ($CaCl_2$) in a desiccator. After 2–3 weeks violet parallelepipeds, unstable in air, were formed. A crystal 0.4 × 0.15 × 0.25 mm was cut from a larger one and placed in a capillary. D_m by flotation in $C_2H_4Br_2/CH_2I_2$. Oscillation and Weissenberg photographs indicated the triclinic system. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (14 reflections, $16 < 2\theta < 28°$), variable $\theta/2\theta$ scan, $4 < 2\theta < 50°$, two standards every 50 reflections, final loss of intensity 26% after 57.5 h of irradiation, mean relative e.s.d. of the control reflections (after correcting for the decay) 3.3%, 2225 reflections measured out of which 2023 had $I \geq 3\sigma(I)$ and of which 1894 were unique, $R_{\text{int}} = 0.027$, index range $h\ 0\rightarrow 8$, $k\ -10\rightarrow 10$, $l\ -12\rightarrow 12$. Structure was solved with *SHELXS*86 (Sheldrick, 1986), and refined with *SHELX*76 (Sheldrick, 1976) in space group $P\bar{1}$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); real and imaginary components of anomalous dispersion included for all non-H atoms. The Nd atoms were located from a Patterson map; the remaining non-H atoms from a difference synthesis; one water H atom was found from a difference synthesis, the other was placed on the basis of assumed hydrogen-bond geometry. Absorption corrections computed after isotropic refinement with locally modified program *ABSORB* (Ugozzoli, 1987) were between 0.64 and 1.19. Final full-matrix least-squares refinement based on F (non-H atoms anisotropic, H atoms with common temperature factor and fixed positional parameters) gave $R = 0.0474$, $wR = 0.0497$, maximum $\Delta/\sigma < 0.001$, $\Delta\rho$ between -2.58 and 1.05 e Å^{-3}, highest peaks around Nd atoms, $w = 1/\sigma^2(F)$, number of parameters = 158.

Discussion. Final atomic parameters are given in Table 1 and the geometry of the Nd coordination in Table 2, together with average bond lengths for the azide anions.* An *ORTEP* view (Johnson, 1976) of the Nd coordination and crystal packing is shown in

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54464 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0250]

0108-2701/92/010004-02$03.00