Short Communication

Thermal Analysis and Crystal Structure of Tetragonal Strontium Oxalate Dihydrate and of Triclinic Strontium Oxalate Hydrate

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The crystal structure of tetragonal strontium oxalate hydrate, $SrC_2O_4 \cdot xH_2O$, which resembles that of tetragonal calcium oxalate hydrate (weddellite), has previously been studied by the single-crystal X-ray diffraction technique,[1] and it was reported that the water of crystallization corresponded to $x = 2.1$, with part of the water molecules (0.1) disordered. Positions of hydrogen atoms were not located. A detailed single-crystal structure analysis of triclinic strontium oxalate hydrate has not previously been made. In an ongoing investigation of the crystal chemistry of oxalates,[2-5] samples of $SrC_2O_4 \cdot xD_2O$ were synthesized. The structures were investigated by the Rietveld method[6] using a neutron powder diffraction pattern and by X-ray single-crystal diffraction analysis.

Experimental

Two crystalline compounds were prepared, tetragonal $SrC_2O_4 \cdot 2D_2O$ and triclinic $SrC_2O_4 \cdot D_2O$. The compounds were formed when a solution of $Sr(NO_3)_2$ (Merck p.a.) in 99.7% D_2O (Hydro) was precipitated with a solution of $C_2O_4H_2 \cdot 2H_2O$ (Ferak p.a.) in 99.7% D_2O. $SrC_2O_4 \cdot 2D_2O$ was precipitated from a solution at room temperature, and $SrC_2O_4 \cdot D_2O$ was precipitated from a boiling solution. The normal hydrates were obtained in a similar way using water as solvent. The purity of the samples was tested with X-ray diffraction powder patterns, measured on a Stoe–Stadi powder diffractometer, using Cu $K\alpha_1$ radiation ($\lambda = 1.540\,598$ Å). The diffractometer was calibrated with an external silicon standard ($a_{Si} = 5.430\,50$ Å). The positions and intensities of the reflections of the powder patterns were in agreement with the values reported on the JCPDS data cards No. 20-1204 for $SrC_2O_4 \cdot 2.5H_2O$ and No. 20-1203 for $SrC_2O_4 \cdot H_2O$. Thermogravimetric analyses were made of the samples using a Stanton Redcroft TG-DTA simultaneous thermal analyser STA 1000/1500 with a heating rate of 5 °C min^{-1} and an argon gas flow. The results of the investigations are displayed in Fig. 1. For $SrC_2O_4 \cdot 2D_2O$ a weight loss of 20.3% at up to 300 °C corresponds to the loss of 2.25 D_2O molecules per formula unit, and a loss of 12.7% at 485 °C corresponds to the formation of $SrCO_3$. This composition was also confirmed from an X-ray powder pattern taken of a sample of strontium oxalate hydrate heated to 600 °C. The water content varies with the preparation of the compound, and in the following the formula $SrC_2O_4 \cdot 2D_2O$ will be used. However, the composition of the sample investigated is in accordance with the neutron diffraction analysis of $SrC_2O_4 \cdot 2.13D_2O$ (see below). The weight loss of 9% up to 300 °C for $SrC_2O_4 \cdot H_2O$ corresponds to the loss of 1.00 H_2O molecule per formula unit.

Neutron powder diffraction patterns of $SrC_2O_4 \cdot 2D_2O$ and of $SrC_2O_4 \cdot D_2O$ were measured at 300 K on the neutron powder diffractometer D2B at the Max von Laue–Paul Langevin Institute.[7] The experimental data for the measured patterns and unit cell parameters for the samples are listed in Table 1. The single-crystal X-ray diffraction data of $SrC_2O_4 \cdot D_2O$ were measured on a Huber four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Experimental data are listed in Table 2.

Results and discussions

$SrC_2O_4 \cdot 2D_2O$. The structure of strontium oxalate dihydrate is tetragonal, space group $I4/m$. The X-ray powder

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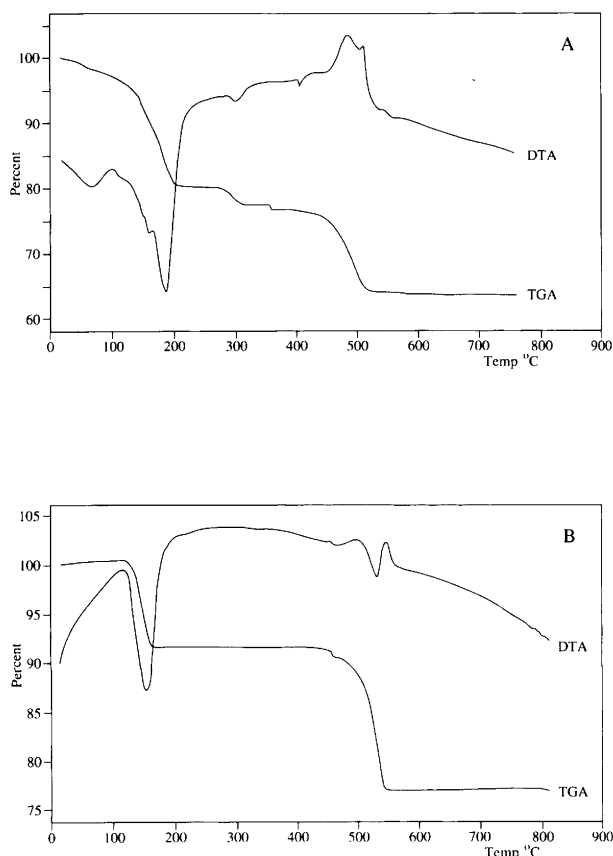* To whom correspondence should be addressed.

Fig. 1. (A) DTA and TGA diagrams for the dehydration and decomposition of strontium oxalate hydrate $SrC_2O_4 \cdot xD_2O$. The dehydration goes in two steps at 180 and 300 °C, respectively, and the decomposition of SrC_2O_4 to $SrCO_3$ takes place at 485 °C. (B) DTA and TGA diagrams for $SrC_2O_4 \cdot H_2O$. The dehydration takes place at 150 °C.

Table 1. Experimental data and unit cell parameters for strontium oxalate hydrate.

	$SrC_2O_4 \cdot 2D_2O$	$SrC_2O_4 \cdot D_2O$
$2\theta_{min}/°$	5.00	5.00
$2\theta_{max}/°$	147.00	147.00
$\Delta 2\theta/°$	0.05	0.05
$\lambda/Å$	1.586(1)	1.594(1)
Max sin $\theta/\lambda/Å^{-1}$	0.60	0.60
Diameter of vanadium container/mm	16	6
$a/Å$	12.7827(8)	6.4877(6)
$b/Å$	12.7827(8)	6.5090(6)
$c/Å$	7.5050(4)	6.4586(6)
$\alpha/°$		108.650(4)
$\beta/°$		109.171(4)
$\gamma/°$		77.277(4)

pattern was decomposed using the program ALLHKL,[8] and the structure factors so obtained were used with the direct method program SIRPOW92,[9] which gave the positions of the atoms Sr, C, OW1 and OW3 (Table 2) in acceptable agreement with the atomic coordinates reported previously for these atoms.[1] Using the model

Table 2. Experimental data and unit cell parameters for triclinic strontium oxalate hydrate, $SrC_2O_4 \cdot D_2O$.

$a/Å$	6.489(2)
$b/Å$	6.514(2)
$c/Å$	6.461(2)
$\alpha/°$	108.63(2)
$\beta/°$	109.48(2)
$\gamma/°$	77.49(2)
Space group	$P\bar{1}$ (No. 2)
Z	2
Size of crystal/mm	$0.05 \times 0.07 \times 0.12$
No. of measured reflections (two standard reflections included for every 50 reflections)	1598
No. of independent reflections	1022
Scan method	ω–2θ
Scan range in θ	$1 + 0.346 \tan \theta$
Density (calcd.)/g cm^{-3}	2.72
Linear absorption coefficient, μ/cm^{-1}	118
Minimum transmission	0.47
Maximum transmission	0.58
R-Value on averages	4.7%

for the structure,[1] the positions of the deuterium atoms of the water molecules were found by packing considerations. The deuterium atoms bonded to the oxygen atoms OW1 and OW2 were each statistically placed in two positions. The water molecule with the oxygen atom OW3 is only partially occupying the site 4e, and its deuterium atoms D3 are statistically placed in site 16i, and occupy this site only partly. The model of the structure was refined using the profile refinement program FullProf,[10] and the atomic coordinates arrived at are displayed in Table 3. The small contributions from the atoms OW3 and D3 are omitted in the formula $SrC_2O_4 \cdot 2D_2O$. Figure 2 is a stereoscopic view of the model of the structure of $SrC_2O_4 \cdot 2D_2O$ along [001].

The structure has one independent strontium atom coordinated with eight oxygen atoms, six oxygen atoms from the oxalate ions and two oxygen atoms from the water molecules. The interatomic distances in this coordination are listed in Table 4. The SrO_8 coordination polyhedron is a three-sided prism with an oxygen atom placed perpendicular to two of the prism surfaces. The oxalate ion is planar with the following distances to the best plane through the six atoms: C: -0.03 Å, C': -0.03 Å, O1: 0.02 Å, O1': 0.02 Å, O2: 0.02 Å, O2': 0.02 Å. (The symmetry element that relates the atom to atom' is a mirror plane at $ab0$.) The deviation from planarity of the oxalate ion is thus marginal. The water molecules take part in the following hydrogen bonds: OW2 has a 2.91 Å contact to O1, and OW1 forms a hydrogen bond of length 2.77 Å to OW3. The oxygen atom OW3 does not have bonds to the strontium atom, and this water molecule is assumed to have a zeolitic nature.[1]

$SrC_2O_4 \cdot D_2O$. The structure of strontium oxalate hydrate is triclinic, space group $P\bar{1}$. A total of 1022 single-crystal reflections with $I > 3\sigma(I)$ were used, and

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Table 3. Atomic coordinates for the structure of $SrC_2O_4 \cdot 2D_2O$, space group $I4/m$, No. 87.

Atom	Site	Occupancy	x/a	y/b	z/c	$B/Å^2$
Sr	8h	0.5	0.3018(8)	0.1955(6)	0.0	0.0(1)
O1	16i	1.0	0.4641(9)	0.2268(8)	0.175(1)	2.3(2)
O2	16i	1.0	0.6435(6)	0.2457(6)	0.183(1)	0.5(1)
C	16i	1.0	0.5534(7)	0.2402(5)	0.106(1)	0.4(1)
OW1	8h	0.5	0.103(1)	0.155(2)	0.0	2.7(3)
OW2	8h	0.5	0.386(1)	0.015(1)	0.0	2.1(3)
OW3	4e	0.13(1)	0.0	0.0	0.190(7)	2.0
D11	16i	0.30(2)	0.082(3)	0.123(3)	0.107(3)	2.0
D12	16i	0.36(2)	0.064(2)	0.198(2)	0.098(3)	2.0
D21	16i	0.53(2)	0.346(1)	−0.027(1)	0.098(2)	2.0
D22	16i	0.23(1)	0.471(2)	0.001(3)	0.040(4)	2.0
D3	16i	0.32(1)	0.026(2)	−0.020(4)	0.324(3)	2.0

$U = 0.119$ Asymmetry parameters $R_P = 5.3\%$
$V = -0.297$ 0.744 $R_F = 8.7\%$
$W = 0.205$ 0.103
$X = 0.042$ 0.134
$Y = 0.042$
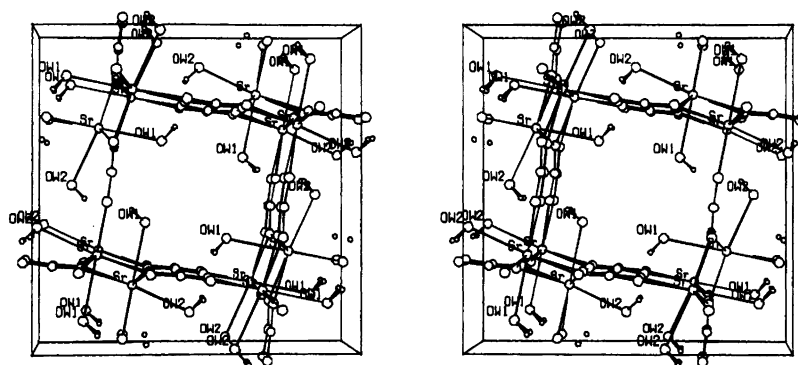
Fig. 2. Stereoscopic view of the structure of $SrC_2O_4 \cdot 2D_2O$ along [001]. For clarity deuterium atoms with lower occupancy are omitted.

Table 4. Interatomic distances (in Å) and angles (in °). Standard deviations on distances are 0.01 Å and on angles are 1.0°.

C-O1	1.27			O1-C-O2	129.1
C-O2	1.29			O1-C-C$^{i'}$	114.2
C-C$^{i'}$	1.59	$i' = x, y, -z$		O2-C-C$^{i'}$	116.5
C$^{i'}$-O1^i	1.27	$i = x, y, -z$		O1^i-C$^{i'}$-O2^i	129.1
C$^{i'}$-O2^i	1.29	$i = x, y, -z$		O1^i-C$^{i'}$-C	114.2
				O2^i-C$^{i'}$-C	116.5
Sr-O1	2.49			OW2-O1	2.91
Sr-O1^i	2.49	$i = x, y, -z$		OW1-OW3	2.77
Sr-OW2	2.55			OW1-D12	1.05
Sr-O2^i	2.55	$i = 1/2 - y, x - 1/2, 1/2 - z$		OW2-D21	1.05
Sr-O2^i	2.55	$i = 1/2 - y, x - 1/2, z - 1/2$			
Sr-O2^i	2.58	$i = y, 1 - x, z$			
Sr-O2^i	2.58	$i = y, 1 - x, -z$			
Sr-OW1	2.59				

the structure was solved by direct methods using the SIR program,[11] which gave the positions of the strontium, oxygen and carbon atoms. The positions of the deuterium atoms of the water molecule were found using a differens Fourier map and packing considerations. The model of the structure was refined in a least squares procedure (LINUS),[12] using scattering contributions from neutral atoms[13] and anomalous scattering contribution from the strontium atom.[14] Anisotropic thermal displacement parameters were refined for the non-hydrogen atoms. Positions and isotropic displacement parameters for the hydrogen atoms were not refined. Unit weights were used. The final R-values obtained were $R(F) = 5.7\%$ and $R(F)_w = 6.9\%$. Atomic coordinates and thermal displace-

ment parameters are listed in Table 5, and selected interatomic distances in Table 6. A stereoscopic drawing of the structure is shown in Fig. 3.

The model of the structure of $SrC_2O_4 \cdot D_2O$ was refined using the neutron powder diffraction data and the profile refinement program FullProf,[10] and the atomic coordinates found are listed in Table 7.

The strontium atom is coordinated with eight oxygen atoms, seven from the oxalate ions and one from the water molecules. The SrO_8 coordination polyhedron has four oxygen atoms in approximately one plane and the

remaining four oxygen atoms in another plane, and the two planes are approximately perpendicular to each other. The planarity of the oxalate ions is deduced from the distances to the best plane through the six atoms of each ion: C1: 0.004 Å, C1[i]: −0.004 Å, O1: −0.001 Å, O1[i]: 0.001 Å, O2: −0.001 Å, O2[i]: 0.001 Å, $i = 2 - x, 1 - y, 2 - z$, and C2: −0.005 Å, C2[i]: 0.005 Å, O3: 0.002 Å, O3[i]: −0.002 Å, O4: 0.002 Å, O4[i]: −0.002 Å, $i = 1 - x, -y, 1 - z$. The deviation from planarity of the two oxalate ions is thus marginal. The water molecule takes part in the hydrogen bonds: O5 has a 2.649(13) Å

Table 5. Atomic coordinates and thermal displacement parameters ($\times 10^3$) for $SrC_2O_4 \cdot D_2O$, X-ray data.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	0.9769(2)	0.1880(2)	0.3058(2)	15(1)	11(1)	15(1)	0(1)	8(1)	6(1)
C1	0.922(2)	0.398(1)	0.892(2)	16(4)	12(4)	22(5)	−3(3)	13(4)	6(3)
C2	0.531(2)	0.055(2)	0.427(2)	19(5)	29(5)	39(6)	−4(4)	18(5)	19(5)
O1	0.985(1)	0.219(1)	0.922(1)	43(5)	12(3)	16(3)	−6(3)	13(3)	7(3)
O2	0.985(1)	0.432(1)	0.710(1)	35(4)	14(3)	15(3)	−6(3)	12(3)	0(3)
O3	0.381(1)	0.170(2)	0.324(2)	15(4)	131(11)	139(12)	19(5)	29(6)	125(10)
O4	0.725(1)	0.018(1)	0.420(1)	14(3)	36(4)	31(4)	−2(3)	9(3)	24(3)
O5	0.581(2)	0.377(3)	0.169(3)	25(5)	151(14)	156(14)	6(7)	18(7)	138(13)

Table 6. Bond lengths (in Å) for $SrC_2O_4 \cdot D_2O$. Standard deviations in parentheses.

Sr–O4	2.560(7)	
Sr–O3[i]	2.565(9)	$i = x + 1, y, z$
Sr–O1[i]	2.570(7)	$i = x, y, z - 1$
Sr–O2	2.576(7)	
Sr–O2[i]	2.578(7)	$i = -x + 2, -y + 1, -z + 1$
Sr–O5	2.590(11)	
Sr–O1[i]	2.591(7)	$i = -x + 2, -y, -z + 1$
Sr–O4[i]	2.603(7)	$i = -x + 2, -y, -z + 1$
C1–O2	1.251(11)	
C1–O1	1.254(10)	
C1–C1[i]	1.581(18)	$i = -x + 2, -y + 1, -z + 2$
C2–O3	1.231(14)	
C2–O4	1.242(12)	
C2–C2[i]	1.541(19)	$i = -x + 1, -y, -z + 1$
O5–O3	2.649(13)	
O5–O5[i]	2.898(21)	$i = -x + 1, -y + 1, -z$
O5–D1	1.08(1)	
O5–D2	0.93(1)	

Table 7. Atomic coordinates for $SrC_2O_4 \cdot D_2O$, neutron powder diffraction data.

Atom	x/a	y/b	z/c
Sr	0.975(1)	0.189(1)	0.308(1)
C1	0.989(1)	0.399(1)	0.897(1)
C2	0.531(1)	0.052(1)	0.426(1)
O1	0.986(1)	0.215(1)	0.920(1)
O2	0.985(1)	0.424(1)	0.715(1)
O3	0.312(1)	0.170(1)	0.317(1)
O4	0.727(1)	0.027(1)	0.422(1)
O5	0.568(1)	0.405(2)	0.180(2)
D1	0.510(4)	0.260(4)	0.175(4)
D2	0.580(4)	0.521(4)	0.310(5)

$U = 0.080$	Asymmetry parameters	$R_P = 4.9\%$
$V = -0.100$	0.122	$R_F = 12.7\%$
$W = 0.138$	0.051	
$X = 0.000$	0.017	
$Y = 0.026$		

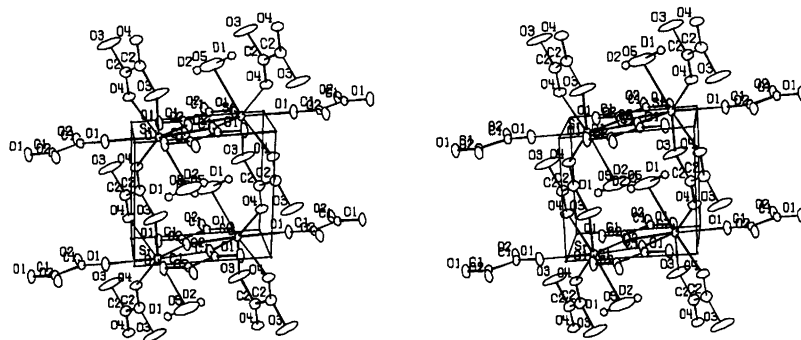*Fig. 3.* Stereoscopic view of the structure of $SrC_2O_4 \cdot D_2O$ along [001].

contact to O3 and has a 2.898(21) Å contact to a symmetry related O5 atom.

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