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The crystal structure of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$

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Abstract: A reinvestigation of the alkali metal thiosulfates has led to the new phase $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$. At first cesium thiosulfate monohydrate was obtained as a byproduct of the synthesis of $\text{Cs}_4\text{In}_2\text{S}_5$. Further investigations were carried out using the traditional synthesis reported by J. Meyer and H. Eggeling. $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ crystallizes in transparent, colorless needles. The crystal structure of the title compound was determined by single crystal X-ray diffraction at room temperature: space group $C2/m$ (No. 12), unit cell dimensions: $a = 11.229(4)$, $b = 5.851(2)$, $c = 11.260(5)$ Å, $\beta = 95.89(2)^\circ$, with $Z = 4$ and a cell volume of $V = 735.9(5)$ Å³. The positions of all atoms including the hydrogen atoms were located in the structure refinement. $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is isotopic with $\text{Rb}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Isolated tetrahedra $[\text{S}_2\text{O}_3]^{2-}$ are coordinated by the alkali metal cations, and in addition they serve as acceptors for hydrogen bonding. For both Cs atoms the shortest distances are observed to oxygen atoms of the $\text{S}_2\text{O}_3^{2-}$ anions whereas the terminating sulfur atom has its shortest contacts to the water hydrogen atoms. Thus, an extended hydrogen bonding network is formed. The title compound has also been characterized by IR spectroscopy. IR spectroscopy reveals the vibrational bands of the water molecules at 3385 cm^{-1} . They show a red shift in the OH stretching and bending modes as compared to free water. This is due both to the $\text{S} \cdots \text{H}$ hydrogen bonding and to the coordination of H_2O molecules to the cesium atoms.

Keywords: cesium thiosulfate monohydrate; crystal structure; IR spectroscopy.

Dedicated to: Professor Wolfgang Jeitschko on the occasion of his 80th birthday.

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1 Introduction

Alkali and alkaline earth metal thiosulfates have been known for many decades. They crystallize in several different structure types containing varying amounts of water of crystallization. In case of the alkaline earth metal thiosulfates water of crystallization seems to be crucial for the formation of crystalline matter.

The structure determination including hydrogen positions from X-ray data often is challenging. The series of the heavier alkaline earth metal thiosulfates was completed with examples for Ca and Sr in 2004 by the reports on $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, and $\text{SrS}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ [1]. The crystal structures of $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ [2–5] and $\text{BaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ [6–8] were determined earlier. The $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{O} \cdots \text{H} \cdots \text{S}$ hydrogen bonding networks therein were determined by neutron diffraction studies [4, 5, 7, 8]. Typically, hydrogen bonding networks involving all water molecules in $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{O} \cdots \text{H} \cdots \text{S}$ bonds with $\text{S}_2\text{O}_3^{2-}$ anions are observed [7].

So far several crystal structures of alkali metal thiosulfate hydrates are well characterized and the hydrogen bonding systems therein have been discussed: $\text{K}_2\text{S}_2\text{O}_3 \cdot 1/3\text{H}_2\text{O}$ [9–12], $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5/4\text{H}_2\text{O}$ [11], and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ [13–16]. A detailed classification of the hydrogen bonds is available for $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. They are divided into four groups: two strong and two weak water–thiosulfate oxygen hydrogen bonds, two water–water, and three water–thiosulfate sulfur hydrogen bonds have been found [13].

Besides the water containing compounds also the anhydrous species were examined [17, 18]. In this context the investigation of the temperature dependent polymorphism of anhydrous $\text{Na}_2\text{S}_2\text{O}_3$ [19] should be mentioned. Röhr and co-workers recently reported on the first crystal structure determination of anhydrous $\text{K}_2\text{S}_2\text{O}_3$ [12].

In contrast to the lighter alkali metal thiosulfates (sodium and potassium) only the crystal structure of the monoclinic $\text{Rb}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been established [12]. The existence of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been known for more than 100 years [20]. However, the crystal structure has not yet been reported in the literature. Herein, we present the crystal structure determination including hydrogen positions from single-crystal X-ray data. The existence of hydrogen bonds in $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is confirmed by IR spectroscopy.

2 Experimental section

2.1 Synthesis

Cesium thiosulfate monohydrate was first obtained as a byproduct of the synthesis of a cesium thioindate [21]. The reaction product was stored in air, and after 24 h at a temperature of about 37°C and high atmospheric moisture, single crystals of Cs₂S₂O₃·H₂O were grown as colorless, transparent needles.

Thereafter cesium thiosulfate monohydrate was synthesized according to the well-known protocol of Meyer and Eggeling [20]. An aqueous solution of cesium carbonate Cs₂CO₃ (99.9%, Sigma Aldrich and Rockwood Lithium) was mixed with an excess of barium thiosulfate BaS₂O₃ (98%, Alfa Aesar) in aqueous solution at 50°C. All starting materials were used as purchased. After stirring and heat treatment the reaction mixture at 90°C for one day, the white precipitate (BaCO₃) was filtered off. Cesium thiosulfate monohydrate remained in solution. This solution was evaporated and subsequently dried in an evacuated desiccator over anhydrous CaCl₂ (≥94%, Roth). Cs₂S₂O₃·H₂O was obtained as a white microcrystalline powder. The purity of the powder was checked by powder X-ray diffraction and vibrational spectroscopy.

2.2 Single-crystal X-ray diffraction and crystal structure determination

Single crystals of Cs₂S₂O₃·H₂O were mounted on glass fibers. The X-ray data were collected at room temperature on a STOE IPDS I diffractometer, using MoK_α radiation (λ = 0.71073 Å, graphite monochromator). For data collection and data processing the Stoe X-Area software was used [22]. The numerical absorption correction was done by X-RED [23] and X-SHAPE [24]. The crystal structure was solved by Direct Methods using SHELXS-97 [25, 26], the structure refinement (full-matrix least-squares on F_o²) was done with SHELXL-97 [25, 26]. Table 1 summarizes the crystallographic data and selected experimental parameters. The atomic coordinates and isotropic displacement parameters are given in Table 2. Table 3 lists the anisotropic displacement parameters. Selected interatomic distances and angles are summarized in Table 4.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-430930.

Table 1: Crystallographic data and details of the structure determination for Cs₂S₂O₃·H₂O.

Cs ₂ S ₂ O ₃ ·H ₂ O	
Crystal data	
Empirical formula	Cs ₂ S ₂ O ₃ ·H ₂ O
Crystal color and shape	Transparent, colorless needles
Crystal system, space group	Monoclinic, C2/m (no. 12)
Pearson code	mC40
Unit cell dimensions (from powder diffraction data)	
a, Å	11.229(4)
b, Å	5.851(2)
c, Å	11.260(5)
β, deg	95.89(2)
Volume V, Å ³	735.9(5)
Z	4
F(000), e	704
Calculated density ρ, g cm ⁻³	3.574
Wavelength λ, Å	0.71073 (MoK _α)
Data collection	
Diffractometer	STOE IPDS I
Monochromator	Graphite
Measuring temperature T, K	293(2)
Measured θ range, °	3.64–31.69
Index ranges hkl	±16, ±7, ±16
Reflections collected	5341
Independent reflections	1265
Data averaging R _{int}	0.0435
Reflections with I > 2σ(I)	920
Completeness to θ = 25°, %	96.9
Absorption coefficient μ, mm ⁻¹	10.412
Absorption correction	X-RED [23] and X-SHAPE [24]
Refinement	
Structure solution	Direct Methods [25, 26]
Refinement	Full-matrix least-squares on F ² [25, 26]
Number of ref. parameters	50
R indices ^a [I > 2σ(I)] R ₁ /wR ₂	0.0263/0.0584
R indices ^a [all Data] R ₁ /wR ₂	0.0395/0.0608
Weighting Scheme Figure citation TAG missing...A ^b	0.0346
Goof ^c on F ²	0.956
Residual electron density ρ, e Å ⁻³	−0.83 ≤ ρ ≤ 1.09

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; ^b w = [\sigma^2(F_o^2) + (AP)^2]^{-1}, \text{ where } P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3; ^c \text{GoF} = S = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}.$$

2.3 Vibrational spectroscopy

Infrared spectroscopic investigations of microcrystalline Cs₂S₂O₃·H₂O were carried out by a Varian FT-IR 670 spectrometer coupled with a GladiATR (attenuated total reflection) unit. Intensities were finally evaluated by the software VARIAN RESOLUTIONS PRO [27].

Table 2: Atom coordinates and equivalent isotropic displacement parameters U_{eq} (\AA^2)^a of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$.^b

Atom	Wykoff	x	y	z	U_{eq}
Cs1	4i	0.22990(3)	0	0.34939(3)	0.0342(1)
Cs2	4i	0.84706(3)	0	0.07426(3)	0.0331(1)
O1	4i	0.8972(5)	0	0.3779(6)	0.054(1)
H	8j	0.933(7)	0.12(1)	0.369(8)	0.10(3)
S1	4i	0.0479(1)	1/2	0.3699(1)	0.0317(3)
S2	4i	0.0339(1)	1/2	0.1888(1)	0.0256(2)
O2	8j	0.0925(2)	0.2927(6)	0.1494(2)	0.0350(6)
O3	4i	0.9056(3)	1/2	0.1465(3)	0.0336(9)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor; ^ball atom sites are fully occupied ($\text{sof} = 1$).

3 Results and discussion

3.1 Crystal structure of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Cesium thiosulfate monohydrate belongs to the large group of compounds, which have been known for a long time and nonetheless basic information as e.g. their crystal structures have never been investigated in detail. Unfortunately, a recent report on the isotypic $\text{Rb}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ [12] does also not provide hydrogen positions. Therefore, we investigated the crystal structure of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and could also obtain the hydrogen positions. Details of the structure determination are displayed in Table 1.

The crystal structure contains $[\text{S}_2\text{O}_3]^{2-}$ anions with almost perfect C_{3v} symmetry. The sulfur–sulfur distance in the thiosulfate ion ($d(\text{S1}–\text{S2}) = 2.028(2) \text{ \AA}$) is identically with the corresponding bond length in $\text{Rb}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ($d(\text{S1}–\text{S11}) = 2.030(2) \text{ \AA}$). The same holds for the S–O interatomic distances, which are $d(\text{S2}–\text{O3}) = 1.470(4) \text{ \AA}$ and $d(\text{S2}–\text{O2}) = 1.470(3) \text{ \AA}$ ($2\times$).

These thiosulfate anions are arranged in layers parallel (001) and the S–S bonds are aligned along [001]. The thiosulfate anions are oriented antiparallel in adjacent

layer. Thus the S–S bonds of a pair of layers and the basal oxygen atoms of the tetrahedra point to each other, see Fig. 1a. The topology of the cesium atoms resembles octahedra. As shown in Fig. 1b, these octahedra are condensed in layers and the thiosulfate anions are embedded therein. Thus, the motif of the CdI_2 structure type results and water molecules are located between the layers. These water molecules are embedded in the crystal structure at the same height in z as the exo-sulfur atoms S1. They form hydrogen bonds to two thiosulfate moieties via the S1 atoms along [010], see Fig. 2. The hydrogen bonds have a strong influence on the crystal growth, thus the needles grow parallel to the b axis.

Two different types of cesium are found in the crystal structure. Cs1 is embedded in the layers of the thiosulfate ions and coordinates to three of these units of one layer. These act as bi-dentate ligands via the exo-sulfur atom and one oxygen atom. In addition, two water molecules from this layer serve as ligands. The coordination sphere is completed by one sulfur atom and one further water molecule from an adjacent layer. The coordination number $\text{CN} = 10$ results, see Fig. 3. By contrast, Cs2 is located between the basal planes of the thiosulfate units. Thus, it is coordinated exclusively by oxygen atoms. Three thiosulfate ions of one layer act as bi-dentate ligands and in addition one water molecule from the same layer is coordinating. Three oxygen atoms of the adjacent thiosulfate layer complete the coordination sphere with $\text{CN} = 10$, see Fig. 4.

3.2 Extended hydrogen bonding system with an O–H...S donor-acceptor interaction, IR spectroscopic investigation of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Röhr already mentioned very short nonbonding distances between terminal sulfur atoms (S1) of adjacent layers in

Table 3: Anisotropic displacement parameters U_{ij} (\AA^2)^a of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	0.0286(1)	0.0378(2)	0.0362(1)	0	0.0037(1)	0
Cs2	0.0323(1)	0.0306(2)	0.0370(1)	0	0.0069(1)	0
O1	0.039(2)	0.053(4)	0.071(3)	0	0.005(2)	0
S1	0.0331(6)	0.0375(8)	0.0249(5)	0	0.0045(4)	0
S2	0.0259(5)	0.0260(7)	0.0254(5)	0	0.0048(4)	0
O2	0.038(1)	0.034(1)	0.034(1)	–0.005(1)	0.008(1)	0.007(1)
O3	0.028(1)	0.039(3)	0.034(1)	0	0.001(1)	0

^aCoefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$.

Table 4: Interatomic distances (Å) and angles (deg) in Cs₂S₂O₃·H₂O.

Atom	-Q	Distance	Angle		
Cs1	-01	3.474(3)	O2-Cs1-O3	77.13(8)	
		3.517(7)	O3-Cs1-O1	72.3(1)	
		3.782(6)		139.0(1)	
	-02	3.110(3)	O2-Cs1-O2	165.5(1)	
			O1-Cs1-S1	57.55(8)	
				64.3(1)	
				67.34(8)	
				67.8(1)	
	-03	3.168(4)		70.06(5)	
				116.0(1)	
			S1-Cs1-O1	119.8(1)	
	-S1	3.554(1)		170.6(1)	
			S1-Cs1-O2	54.57(2)	
			S1-Cs1-S1	171.5(1)	
	-S2	3.590(1)		104.67(5)	
			51.70(4)		
			105.95(3)		
Cs2	-01	3.407(7)	O2-Cs2-O2	109.11(4)	
					124.82(2)
-02	3.176(3)	O2-Cs2-O3	43.2(1)		
			63.0(1)		
			65.2(1)		
			71.41(9)		
			104.08(7)		
			105.52(6)		
			118.04(5)		
			131.59(4)		
			148.62(9)		
			62.04(8)		
			70.58(8)		
			139.91(7)		
			74.13(7)		
			78.36(4)		
			108.41(6)		
44.55(8)					
69.0(1)					
75.58(9)					
75.59(9)					
105.98(9)					
116.58(9)					
131.47(9)					
-03	3.089(1)	O3-Cs2-O3	108.41(6)		
			O3-Cs2-O2	44.55(8)	
-S2	3.751(1)		69.0(1)		
				75.58(9)	
S1	-S2	2.028(2)	S1-S2-O2	108.2(1)	
			S1-S2-O3	107.3(1)	
S2	-02	1.470(3)	O2-S2-O2	111.1(2)	
			O2-S2-O3	110.9(1)	

Rb₂S₂O₃·H₂O [12]. These short distances were discussed as an indication for O-H...S hydrogen bonds. We could refine the hydrogen positions in isotopic Cs₂S₂O₃·H₂O. Thus, we can now prove the assumed expanded O-H...S hydrogen

bonding system along the crystallographic *b* axis, see Fig. 2.

Especially IR spectroscopy is a valuable tool to further investigate the O-H...S donor-acceptor interaction. Lutz published many characteristic OH band shifts of solids with hydrogen bonds [28]. Water molecules can act as both, good hydrogen bonding donors and hydrogen bonding acceptors [28, 29]. Therefore, hydrogen bonds are present in all known solid hydrates. In the presence of hydrogen bonds, the OH stretching modes of the water molecules shift to smaller wavenumbers. The reason is both the smaller force constant and the increased anharmonicity of these vibrations. The half widths of the bands increase and the intensities of the peaks grow. The strength of the hydrogen bonds is correlated with the OH stretching frequencies of the water molecules. The strongest hydrogen bonds, in which water molecules of solid hydrates are involved, are present in hydroxide hydrates because of the very strong proton acceptor strength of OH⁻ ions [29]. The bond length of such strong hydrogen bonds is in the range of 255–280 pm for the O...O distances, and the OH stretching modes are observed at about 2800 and 2150 cm⁻¹. On the other hand, the weakest hydrogen bonds found in solid hydrates are those in NaClO₄·H₂O with OH modes at 3584 and 2641 cm⁻¹ [28, 30].

In the IR spectrum of Cs₂S₂O₃·H₂O (Fig. 5) a shift of the OH stretching mode is observed. The broad peak at 3385 cm⁻¹ (Fig. 5 and Table 5) corresponds to a moderate O-H...S hydrogen bond system.

The proton acceptor strengths of some anions present in solid hydrates can be arranged as follows ClO₄⁻ < NO₃⁻ < ClO₃⁻ < BrO₃⁻ < IO₃⁻ < H₂O < SO₄²⁻ < SeO₄²⁻ < SO₃²⁻ < PO₄³⁻ < OH⁻, S₂O₃²⁻ < SbS₄³⁻ < AsS₄³⁻ < S²⁻ < PF₆⁻ < BF₄⁻ < I⁻ < Br⁻ < Cl⁻ < F⁻ [28, 31–38]. The different strengths of the various proton acceptors are, at least partly, due to the different net charges of the acceptor atoms. For the same acceptors, the strength of the hydrogen bonds depends on the length and arrangement of the hydrogen bonding [28].

The shifts (relative IR shift Δv_{xH} in cm⁻¹: 10–25%) [39, 40] of the OH stretching and bending modes of the water molecules in Cs₂S₂O₃·H₂O correspond to a moderate hydrogen bond system. The interatomic distance of *d*(S...H) = 2.58(9) Å between the donor atoms (S1) and the acceptor molecules (H₂O) also suggests a moderate O-H...S hydrogen bond system in Cs₂S₂O₃·H₂O. The distance between S1 and O1 (*d*(S...O) = 3.396(3) Å) again indicates a hydrogen bond. The bond energy of such predominantly electrostatic interactions is in the range of 4–14 kcal mol⁻¹ [39, 40]. Table 5 summarizes all IR stretching and bending modes of Cs₂S₂O₃·H₂O in comparison to Cs₂S₂O₃·2H₂O and anhydrous Cs₂S₂O₃ [41–46].

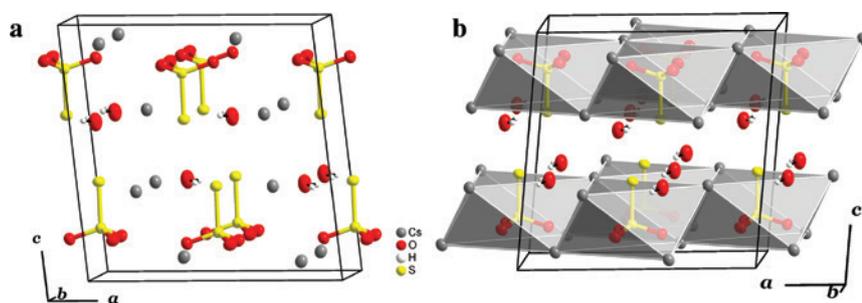


Fig. 1: Section of the unit cell of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

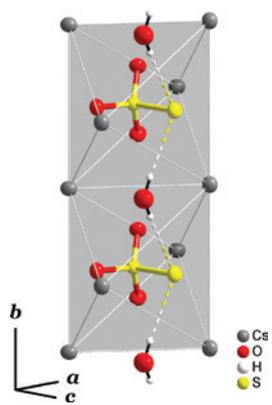


Fig. 2: Structure fragment of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ for highlighting the $\text{S} \cdots \text{OH}$ hydrogen bonds between $\text{S}_2\text{O}_3^{2-}$ moieties and the hydrate water molecules.

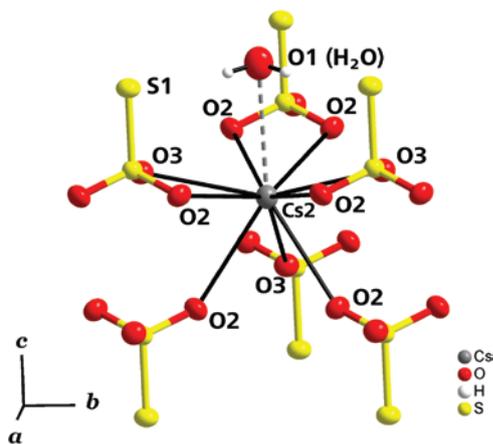


Fig. 4: Exclusively oxygen atoms act as ligands in the first coordination sphere of Cs_2 .

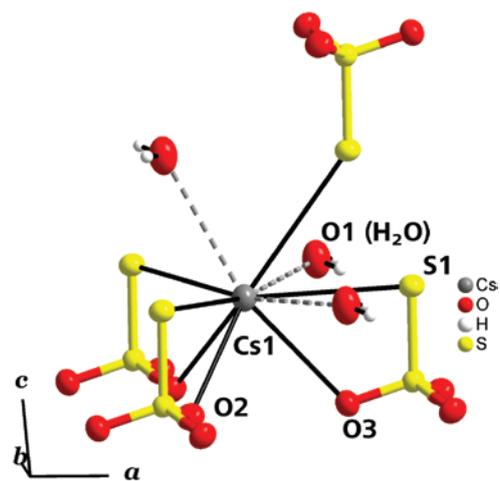


Fig. 3: First coordination sphere of Cs_1 with four sulfur atoms as ligand atoms.

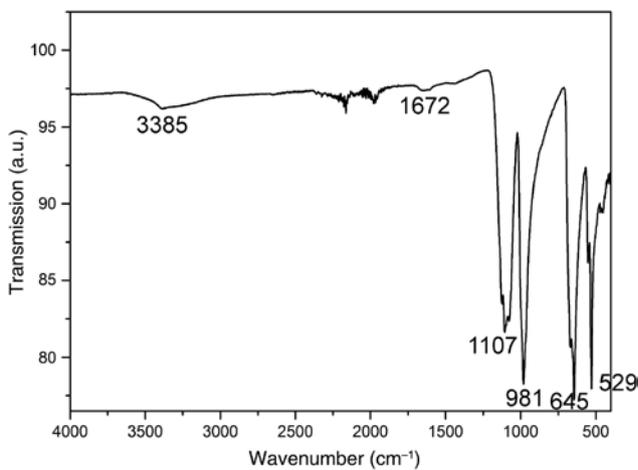


Fig. 5: IR spectrum of $\text{Cs}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ illustrating the red shift of the OH stretching modes at 3385 cm^{-1} .

Table 5: IR stretching and bending modes of Cs₂S₂O₃·H₂O, Cs₂S₂O₃·2H₂O and anhydrous Cs₂S₂O₃ [38–43].

Vibration mode	Cs ₂ S ₂ O ₃ ·H ₂ O	Cs ₂ S ₂ O ₃ ·2H ₂ O	Cs ₂ S ₂ O ₃	
	Wavenumbers (cm ⁻¹)			
Lattice vibrations	50	Not specified	Not specified	
	90			
	107			
	197			
ρ(SO ₃)	Broad band from 365 to 441	334 436	327 336 451	
	ν(SS)			
		δ _{as} (SO)	529	527
δ _{sym} (SO)	645	660	658	
ν _{sym} (SO)	981	995	991	
ν _{as} (SO)	1107	Broad band from 1120 to 1160	1110 1132 1146 1165	
		ν(OH)	3385	Not specified
		δ(OH)	1672	Not specified

4 Conclusion

Cs₂S₂O₃·H₂O is shown to be isotypic with Rb₂S₂O₃·H₂O [12]. The crystal structure resembles an anti-CdI₂ type arrangement with Cs forming layers of octahedra with S₂O₃²⁻ located therein. Water molecules are located between the layers. The hydrogen positions were refined from single crystal X-ray diffraction data. Thus, the O–H···S hydrogen bond system proposed for Rb₂S₂O₃·H₂O by Röhr [12] can now be confirmed by experimental results for the Cs analogue. Additionally, the extended hydrogen bonding system was investigated by IR spectroscopy.

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