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Vibrational spectra of the two hydrates of strontium oxalate



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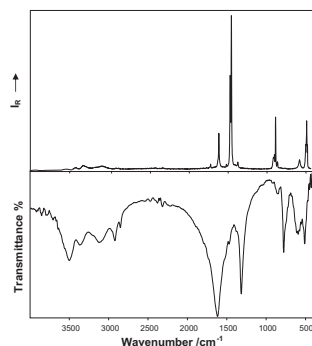
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HIGHLIGHTS

- IR and Raman spectra of $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were recorded and assigned.
- Assignments are discussed in comparison with the related calcium oxalates.
- $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is isomorphous with $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (weddellite).
- $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (whewellite) are not isostructural but are strongly related.
- Structural peculiarities of these oxalates are considered in the discussion.

GRAPHICAL ABSTRACT

$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (space group $P\bar{1}$ and $Z = 8$).



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ABSTRACT

The infrared and Raman spectra of the two hydrates of strontium oxalate, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, were recorded and discussed on the basis of their structural peculiarities and in comparison with the spectra of the related calcium oxalates and other previously investigated metallic oxalates.

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Introduction

As part of our studies of oxalate biominerals [1] and biomineralization processes in plants [1–5], we have performed different studies to attain a wider insight into the general physicochemical properties of metallic oxalates (for a recent review cf. [6]). In this paper, and in order to extend this information, we report the results of an investigation of the vibrational spectroscopic behavior of the two known hydrates of strontium oxalate, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and

$\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. These oxalates are not only important due to their close structural and stoichiometric relation to the two most important biological and geological calcium oxalates [1,6] but also for their recent use as precursors for the synthesis of high temperature superconductors and other oxidic materials [7–10].

Experimental

Synthesis of the investigated compounds

The two compounds were obtained by dropwise addition of a 0.5 M aqueous solution of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ to a 0.5 M aqueous

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solution of strontium nitrate, in equimolecular proportions. $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was precipitated at room temperature whereas $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was obtained from a boiling solution [11]. The precipitates were collected by filtration, washed repeatedly with small portions of cold water and air dried.

The purity of the obtained hydrates was confirmed by X-ray powder diffractometry using a Philips PW 1710 diffractometer and $\text{Cu K}\alpha$ radiation ($\lambda = 1.5425 \text{ \AA}$), as well as by elemental chemical analysis (Carlo Erba EA 1108 elemental analyzer).

Spectroscopic studies

The infrared spectra in the spectral range between 4000 and 400 cm^{-1} were recorded as KBr pellets with a FTIR-Bruker-EQUINOX-55 spectrophotometer. Raman spectra were obtained with a Perkin Elmer FT-Raman RFs 110/s spectrometer, using the 1064 nm line of a solid state Nd:YAG laser for excitation.

Results and discussion

Structural characteristics of the compounds

The structure of $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ belongs to the tetragonal space group $I4/m$, with $Z = 8$ molecules in the unit cell, and it is isomorphic to that of the respective calcium oxalate, the mineral weddellite, even having a small portion of zeolitic water. Therefore it may be better formulated as $\text{SrC}_2\text{O}_4(2+x)\text{H}_2\text{O}$ ($x \leq 0.5$) [12]. The monohydrate, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is triclinic, crystallizing in space group $P\bar{1}$ and $Z = 8$ [11] and, interestingly, it has the same connectivity as the corresponding calcium oxalate, the mineral whewellite, which crystallizes in the monoclinic space group $P2_1/c$ [8].

In both hydrates the coordination of the Sr(II) cations is a distorted square-antiprism conformed by eight oxygen atoms. In the case of the dihydrate, six O-atoms are from four different oxalate moieties and the other two from water molecules. In the monohydrate, only one of these O-atoms is of water and the other seven are from five different oxalate ligands [8,11].

Concerning the oxalate groups, they are practically planar in both structures and in both hydrates they act as bidentate ligands, coordinating to two different Sr(II) ions. Besides, some of the O-atoms of the oxalate units are additionally involved in other Sr–O bonds, as schematically shown in Fig. 1 [8]. $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ contains equal proportions of type A and type B environments, whereas $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ contains only type C oxalate environments [8,13].

A comparison of the structures of the two strontium hydrates [11,12] with those of the related calcium compounds [13] confirms immediately the strong structural analogies mentioned above.

Vibrational spectra of the two hydrates of strontium oxalate

$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

The measured FTIR and FT-Raman spectra of this hydrate are shown in Fig. 2 and the proposed assignments presented in Table 1.

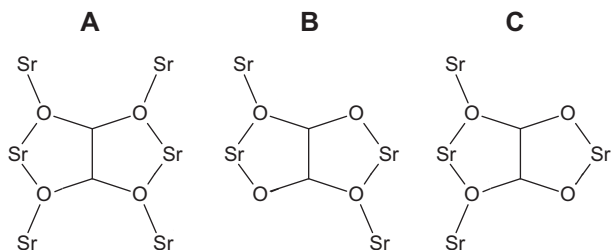


Fig. 1. Modes of oxalate coordination found in the two hydrated strontium oxalates (cf. text).

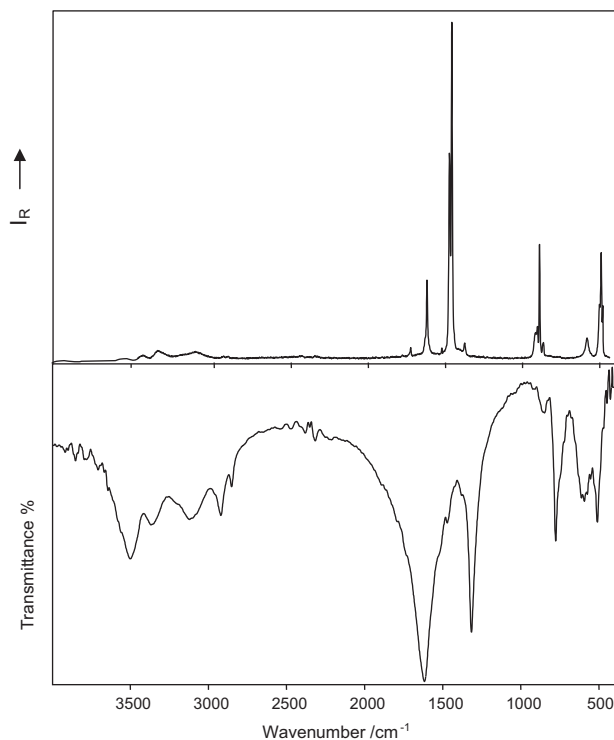


Fig. 2. Raman spectra (above) and FTIR spectra (below) of $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in the spectral range between 4000 and 400 cm^{-1} .

These assignments, which are based on our previous studies mentioned above [6], as well as by comparison with results obtained for the related calcium oxalates, are briefly discussed as follows:

- Vibrations related to the O–H stretchings are appreciably split in the IR spectrum, a fact which has formerly also been observed on the spectrum of whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [1,14–16], and probably originated in the peculiar arrangement and function of the water molecule in this structure [13,17]. In the Raman spectrum, only very weak signals of these vibrations could be found. The corresponding deformational mode, $\delta(\text{H}_2\text{O})$, is surely overlapped by the very strong 1616 cm^{-1} IR band. Notwithstanding, the first overtone of this vibration, probably shifted and intensified by Fermi resonance, could be located in the higher wavenumber region, as is also the case in the IR spectrum of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [14,15,17].
- The weak IR feature at 2850 cm^{-1} probably originates in a combinational mode involving (CO_2) stretching modes. Similar combinations were also found in the case of whewellite [15].
- The antisymmetric (CO_2) stretching vibration appears as a medium intensity Raman band and is the strongest one in the IR spectrum.
- The strongest Raman doublet at $1474/1459 \text{ cm}^{-1}$ has only a very weak IR counterpart at 1460 cm^{-1} . Interestingly, the mentioned splitting of this Raman band is also observed in the case of whewellite [15,18–20].
- The weak Raman band located at 1725 cm^{-1} can be assigned to the first overtone of the very weak 865 cm^{-1} band, as was also suggested in the case of whewellite [19].
- In the spectral range below 1000 cm^{-1} both, the IR and Raman spectra resembles closely the respective whewellite patterns [14–16,18,20]. In this region we have tentatively assigned a librational mode of the water molecule (595 cm^{-1} in the IR, 583 cm^{-1} in the Raman), also by analogy with the whewellite data [17,18]. The weak splitting of the mentioned IR band

Table 1
Comparison and assignment of the vibrational spectra of the two hydrates of strontium oxalate (band positions in cm^{-1}).

$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$		$\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$		Assignment
IR	Raman	IR	Raman	
3500 s	3540 vw, 3430 vw	3625 sh		$\nu(\text{OH})$
3354 m	3350 vw	3450 vs, br	3420 vw	$\nu(\text{OH})$
3122 m	3115 w			$2\delta(\text{H}_2\text{O})$
2918 m	2920 w			$\nu(\text{OH})$
2850 w				cf. text
	1725 w		1736 vw	Overitone, cf. text
1616 vs	1620 m	1621 vs	1619 w	$\nu_{\text{as}}(\text{CO}_2)$
1460 vw	1474 s, 1459 vs	1465 w	1469 vs	$\nu_{\text{s}}(\text{CO}_2) + \nu(\text{CC})$
1366 sh, 1315 vs	1375 vw	1372 sh, 1320 vs	1390 vw	$\nu_{\text{s}}(\text{CO})$
	970 w, 904 w	904 w	903 s	$\nu(\text{CC})$
845 w	890 s, 865 vw		869 vw	$\nu(\text{CC})$
777 s, 730 sh		769 m		$\nu(\text{CC}) + \delta(\text{CO}_2)$
626 sh, 595 m	583 w	586 m	583 w	$\rho(\text{H}_2\text{O})$
509 s	501 w, 490 s	510 m, 485 sh	495 m	$\delta(\text{CO}_2)$
	480 w		490 m	

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

may also be considered as a consequence derived from the structural peculiarities of the water molecules [17]. In the dihydrated metal oxalates of the type $\alpha\text{-M}^{\text{II}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\beta\text{-M}^{\text{II}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, this vibration is usually found at somewhat higher frequencies [6,21] but the water molecules coordinated in these complexes are structurally very different than in the present case [1,22,23].

- No clear evidence was found for the presence of a $\nu(\text{Sr-O})$ vibration. In the calcium oxalates such a mode was suggested to lie at around 500 cm^{-1} [18,24] and, therefore, it must be expected at somewhat lower energy in the present case.

$\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

The recorded FTIR and FT-Raman spectra of this hydrate are shown in Fig. 3 and the proposed assignments, supported by our previous studies as mentioned above [6], and by additional information obtained from the isostructural calcium oxalate, weddellite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, are also included in Table 1. The results are briefly discussed, as follows:

- In this case, the vibrations related to the O–H stretchings of the water molecules appear in the form of a unique, very intense and broad IR band, centered at about 3450 cm^{-1} . As the zeolitic water randomly occupies different sites in the crystal lattice, generating a certain degree of disorder in the crystal structure [13], one may also expect a random distribution of O–H stretching energies, contributing to the observed band broadening. The same spectral behavior is also observed in the IR spectrum of weddellite [16]. Also for this dihydrate, only a very weak Raman counterpart was found in this region, whereas the $\delta(\text{H}_2\text{O})$ mode is surely again overlapped by the strongest IR band (1621 cm^{-1}).
- The last mentioned band corresponds to the antisymmetric (CO_2) stretching mode, which presents only a weak signal in the Raman spectrum.
- Also in this case a very weak Raman band located at 1736 cm^{-1} can be assigned to the first overtone of the very weak 869 cm^{-1} band, by comparison with the results obtained for $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
- Interestingly, the strongest Raman line (1469 cm^{-1}) is not split, as occurs for $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The same behavior is also observed in the Raman spectrum of weddellite [18,20,25]. The IR counterpart of this band is only seen as a weak band at 1465 cm^{-1} .

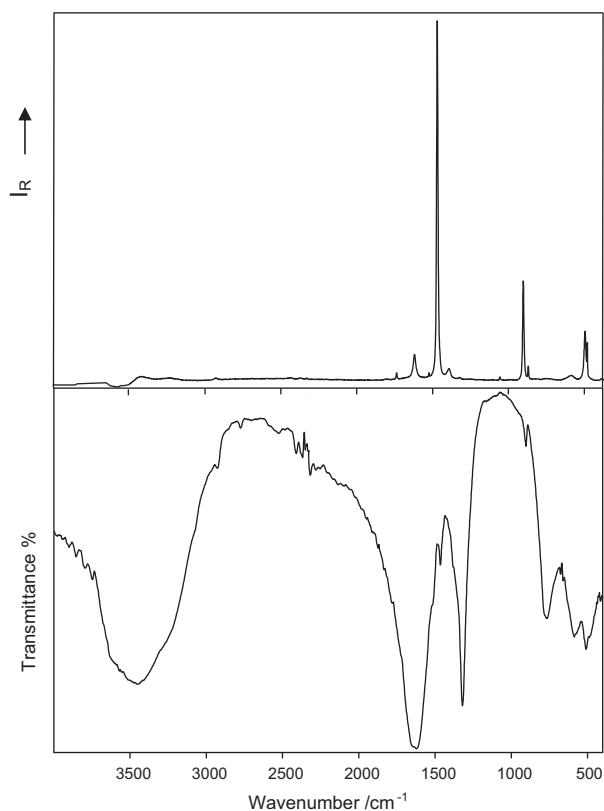


Fig. 3. Raman spectra (above) and FTIR spectra (below) of $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the spectral range between 4000 and 400 cm^{-1} .

- Also in this case the spectral patterns in the lower energy range closely resembles that of weddellite [16,18,25] and, again, we have tentatively assigned a librational mode of the water molecules in the same region as for the monohydrate.

To conclude, the results of this spectroscopic study clearly confirm the strong structural analogies between both hydrates of strontium oxalate, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and also with the corresponding calcium oxalates, whewellite and weddellite. The dihydrates of Sr(II) and Ca(II) are strictly isostructural and, although $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ crystallizes in different

space groups, they present a similar structural arrangement. On the other hand, only small differences in the coordination polyhedra of the divalent cations are found by comparison of the four hydrates. These facts explain the strong similarities between the IR and Raman spectra of the four mentioned oxalates. Major differences are only observed in the IR spectroscopic behavior of the O–H stretching region.

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