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Vibrational spectra of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and CdC_2O_4

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ABSTRACT

The infrared and Raman spectra of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ are recorded and discussed on the basis of their structural peculiarities and in comparison with the spectra of other previously investigated metallic oxalates. The spectra of the anhydrous CdC_2O_4 were also recorded, showing a totally similar spectroscopic behavior, and suggesting a closely related structural arrangement. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Cadmium oxalate trihydrate;
Anhydrous cadmium oxalate;
Infrared spectra;
Raman spectra.

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 trihydrated cadmium oxalate, $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, complemented with additional spectroscopic information for the anhydrous oxalate, obtained by careful dehydration of this hydrate.

EXPERIMENTAL

Samples preparation

The investigated oxalate, $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, was ob-

tained by precipitation, mixing diluted aqueous solutions of cadmium acetate and oxalic acid (this last in a slight excess), working at 65 °C and under continuous stirring. The reacting mixture was heat half an hour more at this same temperature and then the precipitated $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ was separated by filtration, washed with water and air dried^[7]. The purity of the obtained material was confirmed by elemental analysis and X-ray powder diffractometry (JCPDS, file 53-0085).

The anhydrous oxalate was obtained by careful decomposition of the trihydrate at 115 °C, up to constant weight^[8].

Spectroscopic measurements

The infrared spectra in the spectral range between 4000 and 400 cm^{-1} were recorded as KBr pellets with a Bruker IFS 66 FT-IR spectrophotometer. A total of 60 scans were accumulated. Raman spectra, in the range

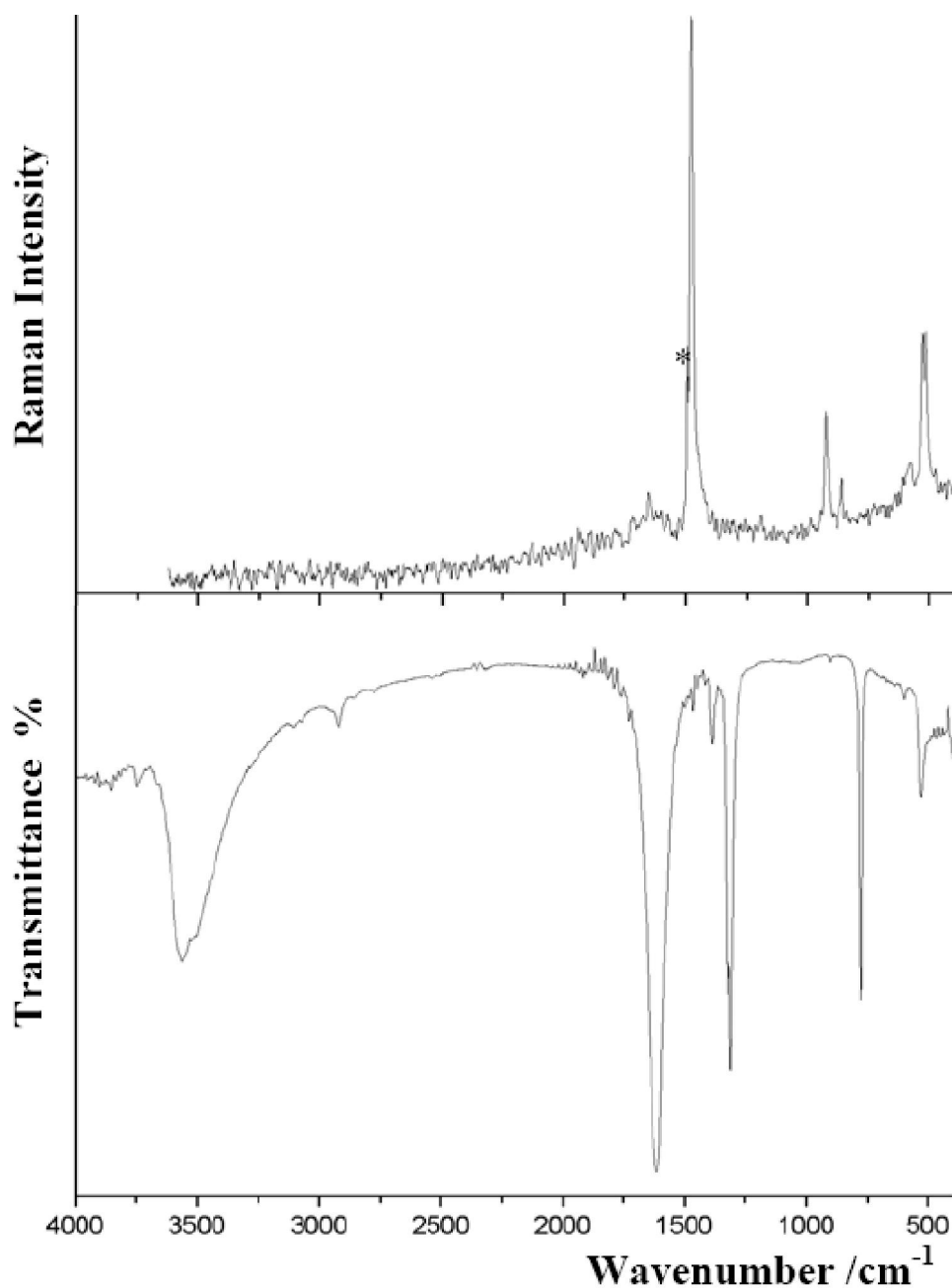


Figure 1 : FT-Raman spectrum (above) and FTIR-spectrum (below) of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (*this band (1492 cm^{-1}) originates in an instrumental noise).

$4000\text{-}100\text{ cm}^{-1}$ were obtained with the FRA 106 Raman accessory of the same Bruker instrument. A total of 60 scans were accumulated, using the 1064-nm line of a solid state Nd:YAG laser for excitation. Spectral resolution was $\pm 4\text{ cm}^{-1}$ in both measurements.

RESULTS AND DISCUSSION

Structural characteristics of the compounds

The polymeric structure of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ is tri-

clinic, space group $P\bar{1}$ and $Z = 2$ and consists of two dimensional arrays formed by a $\text{Cd}_2(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ repeat unit, where both of the symmetry-independent Cd(II) cations are in a seven coordinate oxygen environment, five of these oxygens are from three different oxalate groups and the other from two water molecules. They are also two structurally different oxalate ligands, one of them bridges two Cd(II) centers acting as tetradentate whereas the other two generate Cd_2O_2 units in a different direction.

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TABLE 1 : Assignment of the FTIR and FT-Raman spectra of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and CdC_2O_4 (band positions in cm^{-1})

$\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$		CdC_2O_4		Assignment
IR	Raman	IR	Raman	
3560 vs				$\nu(\text{H}_2\text{O})$
3510 sh				$\nu(\text{H}_2\text{O})$
1611 vs	1660 w	1616 vs	1637 vw	$\nu_{\text{as}}(\text{CO})$
	1478vs,1446sh	1464 vw	1480vs1440w	$\nu_{\text{s}}(\text{CO}) + \nu(\text{CC})$
1383w/1314vs		1378w/1314vs		$\nu_{\text{s}}(\text{CO}) + \delta(\text{OCO})$
	925m,857w		912 s	$\nu(\text{CC})$
777 s		799s/774m	838 m	$\delta(\text{OCO}) + \nu(\text{CC})$
	580 w		615/590vw	δ_{ring}
620 vw,524 m	528/513s	533 m, 510 sh	535w,515s	$\delta(\text{OCO}) + \rho(\text{OCO})$

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

Two additional H_2O molecules of the repeat unit are uncoordinated but involved in the hydrogen bond network present on the structure. The coordination polyhedron of Cd(II) may be described as a distorted pentagonal bipyramid with a water and one oxalate oxygen at the apical positions^{9,10}.

The structure of the anhydrous oxalate, obtained by dehydration of the trihydrate is so far unknown. In this context it should be mentioned that the thermal decomposition of the dihydrated oxalates of the type $\text{M}^{\text{II}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cu}$) allows the generation of anhydrous compounds, which can be obtained in two forms, a disordered one, denominated $\alpha\text{-MC}_2\text{O}_4$, or an ordered one, called $\beta\text{-MC}_2\text{O}_4$ ^[6,11]. In the case of cadmium, a similar $\beta\text{-CdC}_2\text{O}_4$ oxalate can only be obtained by hydrothermal synthesis, but not by the thermolysis of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ^[12].

Infrared and raman spectra of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$

The FTIR and FT-Raman spectra of the trihydrated cadmium oxalate are shown in Figure 1 and the proposed assignment is presented in TABLE 1, and briefly discussed as follows:

- A first comparison of the spectral patterns of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ with those of other previously investigated metallic oxalates^[6] shows a great similarity to the spectra of MgC_2O_4 in the spectral range between 2000 and 400 cm^{-1} ^[13], despite the important structural differences between both oxalates.

- The very strong and broad IR band centered at 3560 cm^{-1} with a shoulder at 3510 cm^{-1} originated in the OH stretching vibrations of the H_2O molecules. No

signals for these vibrations are found in the Raman spectrum. The position of this band suggests the presence of long $\text{O-H}\cdots\text{O}$ bonds^[14,15]. The bending mode, $\delta(\text{H}_2\text{O})$, is surely overlapped by the strong 1611 cm^{-1} band.

- Oxalate modes were assigned on the basis of the MgC_2O_4 spectra^[13] and taking into account also previous results for other metallic oxalates^[6].

- The $\rho(\text{H}_2\text{O})$ mode is probably overlapped by the strong 777 cm^{-1} IR band and the δ_{ring} mode, assigned in the Raman spectrum, probably corresponds to the five-membered chelate rings originated by the tetradentate oxalate ligands^[9].

Infrared and raman spectra of CdC_2O_4

The FTIR and FT-Raman spectra of the anhydrous cadmium oxalate are practically identical to those of the trihydrate in the $2000\text{-}400 \text{ cm}^{-1}$ spectral range. The obtained spectral information is also included in TABLE 1.

Only minor differences were found. The IR mode assigned to $\delta(\text{OCO}) + \nu(\text{CC})$ appears clearly splitted in the anhydrous compound and an inversion in the relative intensities of the last measured Raman band is also observed, in comparison to the trihydrate.

These spectroscopic results suggest that the overall arrangement and geometry of the oxalate groups are not very different in both oxalates.

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