

## Vibrational spectra of a novel selenite $\text{Cd}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$

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Received 4 April 1997, accepted 6 October 1997

**Abstract** The IR and Raman spectra of  $\text{Cd}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$  crystal were recorded and analysed. Bands confirm the existence of  $\text{HSeO}_3^-$  and  $\text{SeO}_3^{2-}$  ions in this crystal. The considerable shifting of the stretching and bending vibrations of the hydroxyl groups and water molecule from the free state values confirm the strong hydrogen bonding in this crystal. ABC bands, characteristic of strong hydrogen bonded systems are observed in the infrared spectrum of this crystal.

**Keywords** FT-IR and FT-Raman spectrum, hydrogen bonding

**PACS No.** 33.20.-t

### 1. Introduction

The crystal chemistry of compounds containing selenite groups  $\text{SeO}_3^{2-}$  and various protonated groups is characterized by the space requirement of the lone pair of electrons [1]. Selenium forms a variety of selenite anions like  $\text{SeO}_3^{2-}$ ,  $\text{HSeO}_3^-$  and  $\text{Se}_2\text{O}_5^{2-}$ , etc. depending on the type of solution used for their preparation. Like other transition elements, cadmium also forms selenites but are very few. The thermal and IR studies of anhydrous cadmium selenites are reported earlier by Gospodinov and Bogolazov [2] and Micka *et al* [3]. Valkonen [4] have reported the synthesis and structures of different cadmium selenites  $\text{CdSeO}_3$ ,  $(\text{NH}_4)_2\text{Cd}(\text{SeO}_3)_2$  and  $\text{Cd}(\text{NH}_3)\text{SeO}_3$ . In the present study, the spectroscopic investigations of cadmium hydrogenselenite selenite were carried out to elucidate the structural role of both anions  $\text{HSeO}_3^-$  and  $\text{SeO}_3^{2-}$  and the nature of hydrogen bonding in it.

### 2. Experimental

Cadmium hydrogenselenite selenite (referred to as CDHS) was prepared as a powdered sample from an aqueous solution containing cadmium acetate and selenious acid [5]. The Raman spectrum of CDHS was recorded using a Bruker FRA 106 FT-Raman spectrometer and FT-IR spectrum was recorded using Bruker IFS 66V FT-IR spectrometer with sample as KBr pellets.

### 3. Crystal structure and factor groups analysis

Cadmium hydrogen selenite selenite,  $\text{Cd}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$  crystallizes in the monoclinic system with space group,  $P2_1/c$  with two formula units per unit cell [5]. CDHS has seven and six coordinated Cd atoms and two different selenite groups, hydrogen selenite and selenite. Both hydrogen selenite and selenite act as bidentate and bridging ligands. There are two crystallographically different Cd atoms in CDHS.

The group theoretical analysis [6] predicts the distribution of irreducible representations at  $k = 0$  excluding acoustic modes as

$$\Gamma_{\text{CDHS}} = 30A_g + 30B_g + 32A_u + 31B_u$$

### 4. Interpretation of the spectra

The spectral analysis of cadmium compound is carried out on the basis of vibrations due to  $\text{HSeO}_3^-$  and  $\text{SeO}_3^{2-}$  ions. The observed internal and external modes are given in Table 1, and the correlation scheme for the internal modes of  $\text{HSeO}_3^-$  and  $\text{SeO}_3^{2-}$  ions in CDHS are given in Table 2. Raman and infrared spectra of the selenite compound are reproduced in Figures 1 and 2.

**Table 1** Spectral data ( $\text{cm}^{-1}$ ) and band assignments of CDHS.

Raman shift ( $\text{cm}^{-1}$ )	IR	Assignments
	3232w	$\nu_{\text{v}}, \nu_1(\text{H}_2\text{O})$
	3126 wbr	
2936vw	2925w	$\nu_{\text{OH}}(\text{A})$
	2196vwbr	$\nu_{\text{OH}}(\text{B})$
	1807w	$\nu_{\text{OH}}(\text{C})$
	1630w	$\nu_2(\text{H}_2\text{O})$
	1248w	$\delta_{\text{OH}}$
	927m	$\gamma_{\text{OH}}$
835vs	831sh	$\nu_3^-(\text{HSeO}_3^-)$ or $\nu_8(\text{SeO}_2)$
814s	800m	$\nu_1(\text{SeO}_3^{2-})$
778m		
736m	742-695vs	$\nu_1^-(\text{HSeO}_3^-)$ and $\nu_1(\text{SeO}_3^{2-})$
705m		
513m	592w	$\nu_3(\text{HSeO}_3^-)$ or $\nu_1(\text{Se-OH})$
	510sh	
441w	456s	$\nu_2(\text{SeO}_3^{2-})$
382vwsh		$\nu_4(\text{SeO}_3^{2-})$ and $\delta(\text{SeO}_2)$
365w		
304vw		
281vw		external modes
235w		
182vw		
142m		
118w		

Relative Intensities : vs-very strong, s-strong, m-medium, vw-very weak, w-weak, wbr-weak broad, sh-shoulder, vwsh- very weak shoulder

**Table 2** Correlation scheme for the internal modes of  $HSeO_3^-$  and  $SeO_3^{2-}$  in  $Cd_3(HSeO_3)_2(SeO_3)_2$ .

$HSeO_3^-$		Free ion symmetry	Site symmetry	Factor group symmetry	
		$C_{3v}$	$C_1$	$C_{2h}$	
24	$6A_1'$		A	$A_g$	9
				$B_g$	9
12	$3A_2''$		A	$A_u$	9
				$B_u$	9

$SeO_3^{2-}$		Free ion symmetry	Site symmetry	Factor group symmetry	
		$C_{3v}$	$C_1$	$C_{2h}$	
8	$6A_1$		A	$A_g$	6
				$B_g$	6
16	$3E$		A	$A_u$	6
				$B_u$	6

The vibrations of  $HSeO_3^-$  can be regarded as the sum of vibrations of  $SeO_2$ , Se–OH and O–Se–OH bonds. A symmetrical pyramidal  $SeO_3^{2-}$  ion is known to be of  $C_{3v}$  symmetry with four fundamental vibrational frequencies, the non-degenerate symmetric stretching and bending modes  $\nu_1$  and  $\nu_2$  at 810 and 425  $cm^{-1}$  and doubly degenerate  $\nu_3$  and  $\nu_4$  at 740 and 372  $cm^{-1}$ , respectively [7]. The grand mean Se–O distance of a free  $SeO_3^{2-}$  ion is 1.709 Å with a root mean square deviation of 0.010 Å and the grand mean O–Se–O angle is 100.2° with a root mean square deviation of 1.3 Å [8]. In the case of hydroselenites, a hydrogen atom is connected to one of the oxygen atoms causing elongation of the corresponding selenium–oxygen bond [9].  $Cd_3(HSeO_3)_2(SeO_3)_2$  has two different anions, hydroselenite and selenite. Se(1) is seen to form the hydroselenite group because one Se–O distance, Se(1)–Se(3) is elongated (1.750 Å) relative to the other Se–O bonds. This stretching is caused by the H atom [5].

In the Raman spectrum of CDHS, a very strong band is observed at 835  $cm^{-1}$  which corresponds to the symmetric stretching vibrations of the  $SeO_2$  groups. The corresponding infrared spectrum gives a shoulder at 831  $cm^{-1}$  in this region [10, 11].

The symmetric stretching vibrations of the  $SeO_3^{2-}$  group gives a strong band at 814  $cm^{-1}$  in the Raman spectrum of CDHS. A medium intense band is obtained at 800  $cm^{-1}$  in the infrared counterpart [12, 13].

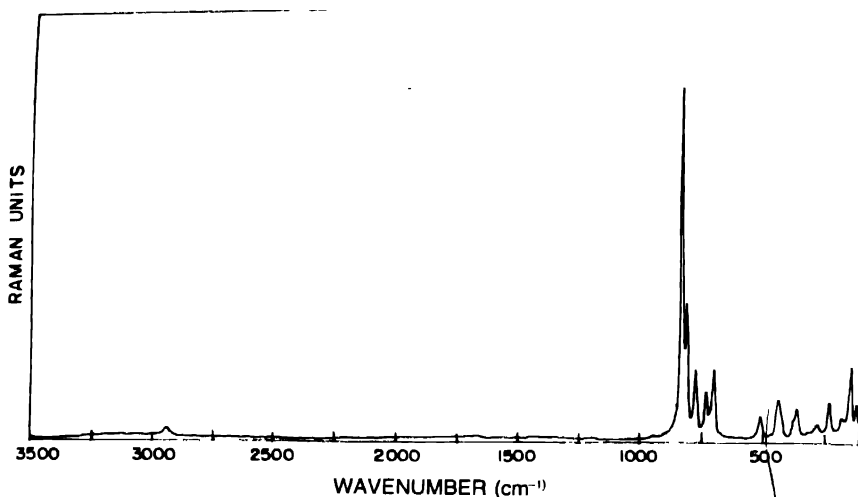


Figure 1. FT Raman spectrum of  $\text{Cd}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$  in the region  $100\text{--}4000\text{ cm}^{-1}$

The bands observed in the  $778\text{ cm}^{-1}$  to  $705\text{ cm}^{-1}$  region is assigned to the asymmetric stretching vibrations of  $\text{SeO}_3^{2-}$  ( $\nu_1\text{SeO}_3^{2-}$ ) and  $\text{HSeO}_3^-$  groups in the Raman spectrum of CDHS. However, the corresponding IR bands are observed as strong broad band in the  $742$  to  $695\text{ cm}^{-1}$ .

The stretching vibrations of hydrogenselenite ( $\nu_1\text{Se-OH}$ ) gives a medium intense band at  $513\text{ cm}^{-1}$  whereas the corresponding infrared band at  $592\text{ cm}^{-1}$  is very weak (Figure 2). These vibrations are found to be at lower wavenumbers in CDHS than the free state values.

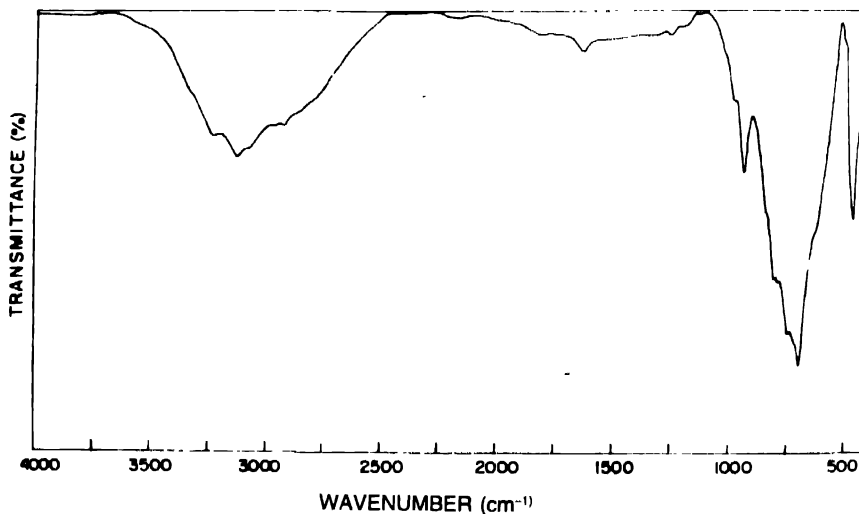


Figure 2. FT-IR spectrum of  $\text{Cd}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$  in the region  $400\text{--}4000\text{ cm}^{-1}$

As expected, the symmetric bending vibrations of  $\text{SeO}_3^{2-}$  ion gives a strong band in the infrared spectrum of CDHS crystal. However, in the Raman spectrum, a weak band at  $441\text{ cm}^{-1}$  is obtained in this region.

Two weak bands are observed for the asymmetric bending modes of the  $SeO_3^{2-}$  and  $SeO_2$  groups in CDHS. Out of the bands observed, the one at  $365\text{ cm}^{-1}$  is of weak intensity whereas the other at  $382\text{ cm}^{-1}$  is of very weak intensity and appeared as a shoulder to the band at  $365\text{ cm}^{-1}$ . The deformation vibrations of  $HSeO_3^-$  ion exhibits only a very weak band in the Raman spectrum of CDHS crystal at  $304\text{ cm}^{-1}$  [14]. The identification of the bands corresponding to the  $SeO_3^{2-}$  and  $HSeO_3^-$  ions in CDHS crystal clearly indicates the co-existence of both the ions.

#### Hydrogen bond vibrations :

In the structural study of CDHS crystal, Koskenlinna *et al* [20] have not mentioned about the strength of hydrogen bonding. But in the stretching region of the OH vibrations,  $\nu_{OH}$  (ABC) bands are observed in the infrared spectra of CDHS crystal. A fairly medium intense broad band observed in CDHS at  $2925\text{ cm}^{-1}$  is assigned as A band. B and C bands are obtained with weak intensity at  $2196\text{ cm}^{-1}$  and  $1807\text{ cm}^{-1}$ , respectively. The appearance of ABC bands in the OH stretching region is due to the strong Fermi resonance between  $\nu(OH)$  and overtones of the  $\delta(OH)$  and  $\gamma(OH)$  vibrations [15, 16]. These bands indicate strong hydrogen bonding in CDHS crystal.

The vibrational frequencies of a free water molecule usually occur at  $3756(\nu_1)$ ,  $3652(\nu_1)$  and  $1595(\nu_2)\text{ cm}^{-1}$ . Depending on the hydrogen bond strength, the stretching mode will shift to lower wavenumbers and bending modes to higher wavenumbers [17]. In the infrared spectrum, two medium broad bands are observed at  $3232\text{ cm}^{-1}$  and  $3126\text{ cm}^{-1}$  for the stretching region of water. The bending mode of water appears around  $1630\text{ cm}^{-1}$ . The considerable shifting of stretching and bending frequencies from those of a free water molecule [17] indicates the presence of strong hydrogen bonding in CDHS crystal.

## 5. Conclusions

Bands confirm the existence of  $HSeO_3^-$  and  $SeO_3^{2-}$  ions in  $Cd_3(HSeO_3)_2(SeO_3)_2$  crystal. The stretching and bending vibrations of hydrogen selenite ion is observed at wavenumber lower in both Raman and IR spectra of CDHS crystal than the free state values indicating strong hydrogen bonding. This is further confirmed from the appearance of ABC bands which is a characteristic of strongly hydrogen bonded systems.

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