JOURNAL OF SOLID STATE CHEMISTRY 73, 184–190 (1988)

Raman Spectral Studies of Dehydration of $Cd(BrO_3)_2 \cdot 2H_2O$

T. DEVANATHAN AND T. K. K. SRINIVASAN*

Structural Chemistry Group, Department of Chemistry, Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras 600036, India

Received April 2, 1987; in revised form September 14, 1987

Raman spectra of single crystal $Cd(BrO_3)_2 \cdot 2H_2O$ have been examined at 298, 337, 343, 388, 403, and 423 K from the fully hydrated state to the totally anhydrous one. The spectra reveal changes in the region ν_1–ν_3 of the bromate ion which have been interpreted on the basis of a possible change in site symmetry for the bromate ion from C_1 to C_3 during dehydration. The X-ray powder pattern of the dehydrated sample has been satisfactorily indexed on the basis of a hexagonal unit cell. © 1988 Academic Press, Inc.

Introduction

There has been a growing interest in understanding the nature and role of water in the crystallization of hydrated crystals. The anion–water interaction involving hydrogen bonding affords stability to the structures of these compounds. Hydrated metal halates have been the subject of many spectral studies (*1–3*). However, not many systematic spectral investigations on the process of dehydration have been carried out and the physical properties of these compounds in the anhydrous state have not been extensively studied.

The residue after dehydration of a simple hydrate may consist of a lower hydrate or an anhydrous salt. In most cases, the dehydrated residue transforms to give a new solid phase. Vibrational spectroscopy is a sensitive technique for detecting subtle structural changes. Infrared and Raman spectra of $Ba(ClO_3)_2 \cdot H_2O$ and $Ba(ClO_3)_2$ revealed that the lattice structure of anhydrous $Ba(ClO_3)_2$ differs from that of the monohydrate (*3*). The two different structures have been characterized by X-ray investigations as well.

A detailed vibrational analysis of $Cd(BrO_3) \cdot 2H_2O$ using Raman and infrared techniques has been carried out and the results are published elsewhere (*4*). The aim of the present study was to examine the structural changes taking place in $Cd(BrO_3)_2 \cdot 2H_2O$ as the water of hydration is gradually lost on thermal treatment. Preliminary results were presented recently (*5*). In addition, the x-ray powder diffraction pattern of anhydrous $Cd(BrO_3)_2$ has been characterized in order to substantiate the spectral results.

Experimental

$Cd(BrO_3)_2 \cdot 2H_2O$ was prepared by the chemical reaction between stoichiometric quantities of cadmium sulfate and barium bromate according to the equation:

---

* To whom correspondence should be addressed.

0022-4596/88 $3.00

$$3Ba(BrO_3)_2 \cdot H_2O + 3CdSO_4 \cdot 8H_2O \rightarrow 3Cd(BrO_3)_2 \cdot 2H_2O + 3BaSO_4 + 5H_2O$$

$Cd(BrO_3)_2 \cdot 2H_2O$ crystallized out as needle-shaped transparent crystals from the filtrate and its formula was confirmed by thermogravimetric analysis. The needle direction was identified as the *c*-axis. Orientation of the crystal was determined by polarizing microscope and X-rays.

Raman spectra were recorded using a standard 90° configuration. The laser employed was a Spectra Physics Model 165 Argon Ion Laser operating at 200 to 250 mW power on the 5145-Å line. Scattered radiation was analyzed with Cary-82 triple monochromator fitted with polarizer and an analyzer. The frequencies obtained were correct to within ± 1 cm^{-1}. The far infrared spectra were recorded on a Polytec FIR-30 spectrometer using polyethylene pellets.

An all-glass conventional-type liquid nitrogen container cell provided with heating coil was used for temperature-dependent Raman spectral studies. Thermocouple readings were used to estimate the sample temperatures. Temperatures measured with the thermocouple were within ± 1 K.

Differential scanning calorimetric (DSC) studies were carried out with a Perkin–Elmer DSC-2 instrument.

The X-ray diffraction patterns were recorded using a Philips PW1050 diffractometer. Copper $K\alpha$ was used as the source for X-rays.

Results and Discussion

The crystal structure of $Cd(BrO_3)_2 \cdot 2H_2O$ at room temperature (298 K) was reported earlier (*6*, *7*). The crystal belongs to the orthorhombic space group $P_{2_1 2_1 2_1}(D_2^4)$. The unit cell has four molecular units and each atom is in general position. The cell dimensions are: $a = 12.49$ Å, $b = 6.17$ Å, $c = 9.23$ Å, volume = 712.09 Å^3, $D_m = 3.58$ cm^{-3}, $Z = 4$.

A combination of graphical and analytical methods were resorted to in order to characterize the powder pattern of the anhydrous sample. Table 1 summarizes the analysis of the pattern. The pattern was satisfactorily indexed on the basis of a hexagonal symmetry and a least-squares refinement was carried out using Cohen's method (*8*). The analysis was verified using graphical methods. Hull–Davey charts were used for the purpose.

The following results pertain to this analysis: $a = 11.19$ Å, $c = 8.71$ Å, $\gamma = 120°$, volume = 946.54 Å^3, $D_m = 3.91$ g cm^{-3}, $z = 6$. However, neither the exact space group nor the point group symmetry could be unambiguously established and selection rules predicted for the altered structure from the powder diffraction data. Furthermore, it was difficult to obtain single crystals of anhydrous $(Cd(BrO_3)_2$.

The temperature dependence of the stretching modes of the bromate ion in $Cd(BrO_3)_2 \cdot 2H_2O$ are shown in Fig. 1. Figure 2 represents the changes in the Raman spectra in the region 1000–10 cm^{-1} at 90, 298, and 423 K. The infrared spectra of the

TABLE I

X-RAY POWDER DIFFRACTION PATTERN OF ANHYDROUS CADMIUM BROMATE

2θ (observed) (deg.)	2θ (calculated) (deg.)	*hkl*
15.75	15.82	110
24.45	24.27	120
27.20	27.58	030
30.70	30.78	003
32.18	32.16	013
36.06	36.04	203
39.28	39.36	132
40.55	40.53	320
43.85	44.02	411
46.10	45.98	313
48.80	48.78	330
51.50	51.57	052
57.10	56.96	600

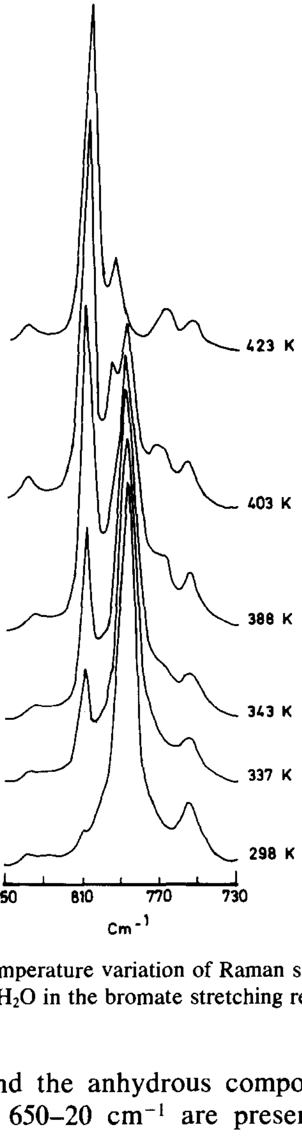

FIG. 1. Temperature variation of Raman spectra of $Cd(BrO_3)_2 \cdot 2H_2O$ in the bromate stretching region.

hydrate and the anhydrous compound in the range 650–20 cm^{-1} are presented in Fig. 3.

The classification of the internal modes of BrO_3^- belonging to the c_{3v} point group are as follows:

ν_1 = BrO_3^- symmetric stretch;
ν_2 = BrO_3^- symmetric bend;
ν_3 = BrO_3^- asymmetric stretch;
ν_4 = BrO_3^- asymmetric bend.

At 298 K, the ν_1 band of BrO_3 is observed with strong intensity at 788 cm^{-1} while the ν_3 band at 810 cm^{-1} appears as a weak feature. As the temperature is increased from 298 K, there is a gradual increase in the intensity of the band at 810 cm^{-1} while that at 788 cm^{-1} decreases slowly in intensity. At 388 K, the bands at 788 and 810 cm^{-1} are of equal intensity. On further heating, the single crystal becomes an aggregate of small crystals. At 403 K, a weak shoulder at 795 cm^{-1} develops on the high-frequency side of the band at 788 cm^{-1} and the intensity of the latter is considerably less than that at 810 cm^{-1}. At this point all the water is lost as seen by the disappearance of the bands in the (OH) stretching region. Also the ν_3 band attains high intensity at this temperature. On further heating to 423 K, the band at 788 cm^{-1} shifts to 795 cm^{-1}. A band at around 771 cm^{-1}, which was present as an inflection on the low-frequency side of the band at 788 cm^{-1} at 298 K, separates out and appears as a band at the same position with weak intensity at 423 K. This band at 771 cm^{-1} is probably due to a combination. A band at 753 cm^{-1} is observed at 298, 90, and 423 K. This band is assigned to the BrO stretching vibration in the coordination polyhedra of Cd^{2+} (*4*). On cooling from 423 to 298 K, the original spectrum consisting of the bands at 810 and 788 cm^{-1} is obtained, indicating thereby that the changes occurring in the band positions with temperature variation are reversible and thus independent of water molecules. However, the intensities of the bands do not revert to the initial pattern present in the spectra of the hydrate (298 K). The ν_1 band at 788 cm^{-1} appears with significant intensity, but it is still not as strong as the ν_3 band at 810 cm^{-1}. The ν_2 nondegenerate mode at 441 cm^{-1} is unaffected by thermal treatment.

The ν_4 band at 298 K shows removal of degeneracy and the site splitting is observed at 393 and 372 cm^{-1}. Splittings of a similar order of magnitude have been observed for other bromates (*9*). However, only an intense and broad band around 393

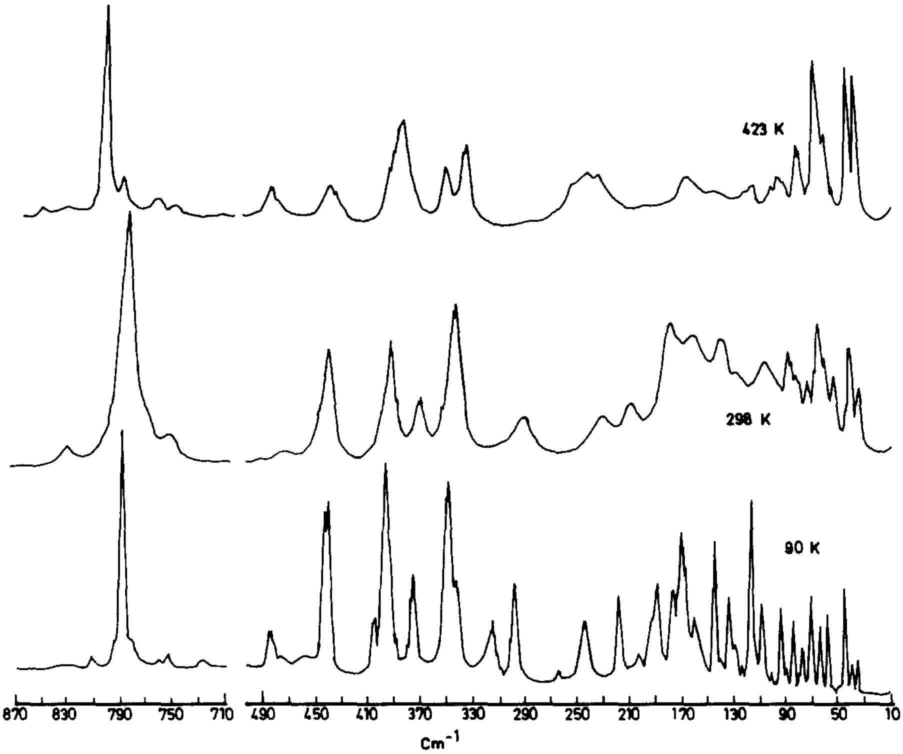

FIG. 2. Raman spectra in the bromate internal mode region and external modes of $Cd(BrO_3)_2 \cdot 2H_2O$ recorded at 423, 298, and 90 K.

cm^{-1} is present at 423 K indicating thereby that the degeneracy is restored at the high temperature.

A band at 355 cm^{-1} which was not present at 298 K appears at 423 K. The position of this band is close to that at 358 cm^{-1} ascribed to the ν_4(E) mode of BrO_3^- at a C_3 site in $NaBrO_3$ (*10*). The ν_4(E) mode in the present system is already attributed to the band at 393 cm^{-1}. The position of the band at 355 cm^{-1} is too far (40 cm^{-1}) apart from that at 393 cm^{-1} to account for a site splitting based on C_1 point symmetry in the crystal. Furthermore, the selection rules pertaining to site and factor groups in the anhydrous sample are not known. The CdO stretching was observed at 320 cm^{-1} in the Raman spectra of $Cd(NO_3)_2 \cdot 4H_2O$ (*11*). Since the Cd–O bond lengths in $Cd(BrO_3)_2 \cdot 2H_2O$ (Cd–OBr, 2.33–2.54 Å) and in $Cd(NO_3)_2 \cdot 4H_2O$ (Cd–ON, 2.44–2.59 Å) are very similar, it is more probable that the band at 355 cm^{-1} is due to CdO stretching as assigned in our earlier publication (*4*).

Raman spectra at 423 K compared to that at 298 K shows an increased intensity of the bands in the lattice region. The spectrum of the dehydrated compound at 423 K reveals the absence of bands at 56, 75, 208, and 291 cm^{-1} observed at 298 K. These are either due to the disappearance of the lattice modes of water or a change in the selection rules due to an altered lattice structure at 423 K. The band around 138 cm^{-1} is extremely weak in the spectrum at 423 K. Two bands observed at 298 K at 208 and 232 cm^{-1} collapse into a broad band around 240 cm^{-1} at 423 K while the bands at 157 and 176 cm^{-1} appear as a single broad feature at 163 cm^{-1} in the spectrum of the an-

FIG. 3. Infrared spectra in the range 650–20 cm^{-1} of (I) hydrated and (II) anhydrous cadmium bromate recorded at 298 K.

hydrous compound. The remaining bands present in the spectrum at 423 K are evidently due to the lattice modes of BrO_3^- and Cd^{2+}. The infrared spectra of the dehydrated compound in the region 650–20 cm^{-1} revealed better resolved bands compared to the hydrate. However, no significant changes were observed.

The spectral observations reveal that loss of water of hydration in $Cd(BrO_3)_2 \cdot 2H_2O$ results in an alteration of the structure. However, the structure of the anhydrous compound has not been characterized, unlike barium chlorate (*12*). A structural change can take place either due to a change in temperature or due to a change in chemical composition. Differential scanning calorimetric studies indicated loss of water at 393 K. Therefore, the spectral changes on dehydration are principally due to a change in chemical composition, namely, loss of water.

The frequency changes in the stretching region of BrO_3^- with temperature are completely reversible and thus the changes are not exclusively the result of water loss but also may be due to a change in site symmetry. The sharp features of the bands in the bromate stretching region and in the lattice region below 100 cm^{-1} reveal a relatively ordered environment for the bromate ion on dehydration while the librational modes show considerable broadening. This broadening may be a consequence of clustering of the librational modes of BrO_3^- on dehydration.

Changes in site symmetry are sensitively indicated in the Raman spectra by the internal modes (*13*). Considerable differences are shown between the spectra at 298 and 423 K in the ν_1–ν_3 region. As has been mentioned earlier the ν_3 mode becomes intense at 423 K. In addition, the compound is no longer a single crystal, the polarization characteristics of the ν_3 mode could not be definitely established, and the infrared spectra are not well resolved. The strong intensity and sharpness of the band at 810 cm^{-1} and the weak nature of the band at 795 cm^{-1} at 423 K suggest that the former has acquired more symmetric character. A similar band around 815 cm^{-1} in the mixed compound of $NaBrO_3$ and $NaClO_3$ in the C_3 site is shown to be accidently degenerate and the intensity increase has been interpreted as due to mode mixing (*14*).

The similarity between the Raman spectra of cadmium bromate at 423 K and that of the mixed halates (*14*) at room temperature in the bromate stretching region indicate that in cadmium bromate a mixing of the ν_1 and the ν_3 modes appears to take place in the C_3 site which gives rise to an increase in the intensity of the ν_3 mode at 423 K.

The ν_4 mode is a sensitive probe which reflects changes in site symmetry as the crystal undergoes transformation from one phase to another (*13*). It is found to regain its degeneracy a 423 K while the nondegenerate ν_2 mode remains unaffected at 423 K.

In the lattice region, except for the disappearance of certain bands, the positions of the bands below 100 cm^{-1} observed at 298 K remain unaltered on dehydration.

The crystal structure of $Cd(BrO_3)_2 \cdot 2H_2O$ at 298 K (*6, 7*) revealed that the geometry of the bromate ion is only slightly distorted from the pyramidal configuration, thermal treatment would have provided sufficient energy for a change in site symmetry, and, furthermore, vacancies created by loss of water during dehydration would facilitate such a change. The number of molecules in the unit cell are different in the hydrated ($Z = 4$) and anhydrous compound ($Z = 6$). Comparing the densities, the density of anhydrous cadmium bromate is greater than that of the hydrate, which denotes that the packing is more efficient after dehydration.

In the present study, since the structure of the anhydrous compound has been found to conform to a hexagonal symmetry, an average C_3 site symmetry for the BrO_3^- is plausible. The absence of mutual exclusion between the infrared and the Raman spectra indicates the nonexistence of a center of inversion. As discussed earlier, temperature-dependent Raman spectra of the internal modes could be satisfactorily interpreted assuming a C_3 site for BrO_3^-. Therefore both spectral and X-ray studies made thus far indicate a possible change in site symmetry for BrO_3^- from the general C_1 site to a C_3 site in the anhydrous compound.

Acknowledgments

The authors thank Dr. G. Sreenivasamurthy, Department of Physics, Indian Institute of Technology, Madras, for useful suggestions in the analysis of the powder pattern. One of us (T.D.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for providing a research fellowship.

References

1. H. D. Lutz and H. J. Kluppel, *Ber. Bunsen–Ges Phys. Chem.* **79,** 98 (1975).

2. J. E. Bertie, A. M. Heyns, and O. Oehler, *Canad. J. Chem.* **51,** 2275 (1973).

3. H. Vargas, J. Pelzl, J. Laugier, D. Dautreeppe, and J. P. Mathieu, *J. Magn. Reson.* **20,** 269 (1975).

4. T. Devanathan and T. K. K. Srinivasan, *J. Raman Spectrosc.* **18,** 525 (1987).

5. T. K. K. Srinivasan and T. Devanathan, "Proceedings of the Tenth International Conference on Raman Spectroscopy, Eugene" (1986).

6. V. V. Satyanarayana Murty, Ph.D. Thesis, Indian Institute of Technology, Madras (1980).

7. N. I. Golovostikov, *Sov. Phys. Crystallogr.* **24,** 135 (1979).

8. M. U. Cohen, *Rev. Sci. Intrum.* **6,** 68 (1935); **7,** 155 (1936).

9. W. Eckers and H. D. Lutz, *Spectrochim. Acta Part A* **41,** 1321 (1985).

10. A. D'Andrea, B. Fornari, G. Mattei, M. Pagannone, and M. Scrocco, *Phys. Status Solidi B* **53,** 577 (1972).
11. D. W. James, M. T. Carrick, and W. H. Leong, *Aust. J. Chem.* **31,** 1189 (1978).
12. L. S. G. Cancella, G. M. Gualberto, C. A. S. Lima, H. Vargas, and J. Pelzl, *J. Chem. Phys.* **68,** 2844 (1978).
13. R. B. Wright and C. H. Wang, *J. Phys. Chem. Solids* **34,** 787 (1973).
14. H. F. Nichols and R. Frech, *J. Chem. Phys.* **71,** 1016 (1979).