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# Carbon Dioxide Stably Caged in an Amorphous Barium Tungsten Oxide up to 500°C

TETSUICHI KUDO AND HIROSHI OKAMOTO

*Central Research Laboratory, Hitachi Ltd., Kukubunji, Tokyo 185, Japan*

KAZUKO MATSUMOTO

*Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 160, Japan*

AND YUKIYOSHI SASAKI

*Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

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A kind of tungsten-based peroxohetero(carbon)polyacid, synthesized through the reaction of WC with $H_2O_2$, reacts with $Ba(NO_3)_2$, giving an amorphous barium salt in which carbon forms $CO_3$ groups. By heating the salt at 300°C, almost all of the $CO_3$ is transformed into molecular $CO_2$, which is caged in an amorphous framework of the Ba salt. Its $\nu_2$ vibration spectrum lacks a fine structure due to molecular rotation, suggesting that each $CO_2$ is closely surrounded by the framework. On the other hand, Cs salt shows no caging phenomenon. The empirical formula of the compound caging $CO_2$ (as well as $O_2$) is expressed by $4BaO \cdot 12WO_3 \cdot \frac{1}{2}O_2 \cdot 2CO_2$. On further heating, these caged molecules are released when crystallization occurs around 520°C. © 1987 Academic Press, Inc.

## Introduction

One of the authors has reported that tungsten carbide was dissolved in a hydrogen peroxide solution, giving a strongly acidic solution, and that a pale yellow noncrystalline solid solidified from the solution was a kind of tungsten-based heteropolyacid with carbon as a heteroatom (denoted hereafter by CW-HPA) (*1*, *2*). Both $^{13}C$ NMR and infrared spectra showed that carbon in the heteropolyanion may be in the form of a $CO_3$ group (as far as the nearest oxygens are concerned).

It has also been found that a carbon-free isopolyacid (W-IPA), which is analogous to CW-HPA, can be similarly synthesized by the direct reaction of metallic W with a $H_2O_2$ solution (*2*). The results of spectroscopic studies including $^{183}W$ NMR ($^{183}W$ shifts from 1 *M* $Na_2WO_4$: $-185.5$ ppm for CW-HPA and $-186.6$ for W-IPA) suggests that CW-HPA and W-IPA are almost identical to each other in terms of polyanion structure, except that the latter does not contain carbon heteroatoms. The relationship between them may be similar to that between $H_3[PW_{12}O_{40}]$ and $H_6[H_2W_{12}O_{40}]$. It should be noted that these two acids have peroxo(O–O) groups in their polyanions

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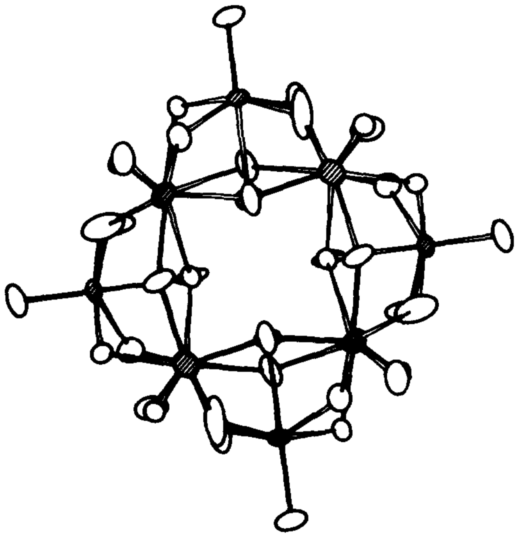

FIG. 1. Structure of the polyanion in the $K^+$ 18-crown-6 salt of CW-HPA. Hatched and open ellipses are W and O atoms, respectively. The carbon atom is in the central cavity though not shown. The determination of its exact position is under way.

(*2*), and that their $^{183}W$ chemical shifts are considerably different from those reported for conventional 12-heteropolytungstates (*3*).

Recently we found that CW-HPA and W-IPA form insoluble salts with some cations, such as $Cs^+$, $Ba^{2+}$, $K^+$ 18-crown-6, etc., having large ionic diameters. The single-crystal X-ray diffraction from the $K^+$-crown salt, $(KC_{12}H_{24}O_6)_4 \cdot (CW_{12}O_{40}) \cdot 2H_2O$, showed that its polyanion has a slightly distorted Keggin structure, as shown in Fig. 1, and the carbon heteroatom occupies the central tetrahedral cavity (*4*, *5*). Though all the salts with inorganic cations in the present study were obtained in an amorphous phase, their polyanions are likely to have a structure basically similar to that of the crown salt.

We found that amorphous intermediate compounds, which are derived from thermal decomposition of the CW-HPA and W-IPA Ba salts, cage most of the $CO_2$ and/or $O_2$ molecules generated by decomposition of the polyanions. The purpose of the present article is to report on this unique caging phenomenon of carbon dioxide and/or oxygen molecules.

## Experimental

### *Preparation of Compounds*

As previously described (*1*), tungsten carbide powder was dissolved in 15% $H_2O_2$, yielding an almost colorless, strongly acidic solution. The solution was then dried at room temperature after removing the small amount of undissolved impurities by filtration and decomposing excess $H_2O_2$ catalytically with platinized Pt nets. A pale yellow amorphous glassy material (CW-HPA) was obtained. The C : W ratio in CW-HPA is dependent on the synthetic conditions, especially on the aging time from dissolution of WC to solidification. A 1 : 6 compound is obtained if the solution is dried within 1 day. However, the ratio was 1 : 12 (previously reported composition (*1*)) when dried after about 10 days. Carbon-free isopolyacid (W-IPA) was obtained similarly using metallic W powder instead of WC. This material was also amorphous and its appearance was almost the same as CW-HPA.

Barium salts (Ba CW-HPA and Ba W-IPA) were precipitated by adding a CW-HPA or a W-IPA solution into a saturated $Ba(NO_3)_2$ solution at room temperature. The precipitates were then rinsed with a large amount of water at room temperature and dried at 50°C for 5 hr in air. The salts of Cs, Rb, Pb, and Ag were obtained similarly using concentrated solutions of CsCl, RbCl, $Pb(NO_3)_2$, and $AgNO_3$.

### *Chemical Analysis*

The W content in CW-HPA and W-IPA was determined from the weight of $WO_3$ given by heating at 700°C in air. The W content in the salts was analyzed by inductively coupled Ar plasma spectroscopy (ICPS) using their $H_2O_2$ solutions. These salts are quite soluble in aqueous solutions of $H_2O_2$, and the resultant solutions of Ba · CW-HPA, etc., were colorless and acidic.

The carbon content was determined from $CO_2$ generated during sample heating at 700°C in oxygen using a gas chromatography CHN analyzer (026-type, Hitachi, Ltd.).

The peroxo(O–O) content was measured using conventional iodometric titration of $I_2$ produced by the reaction of the present acids (or salts) with KI in an aqueous solution phase (Ba-CWHPA, etc., has a solubility of approximately 0.5 mg/10 ml $H_2O$).

The Ba and Cs content in the salts was determined by ICPS and atomic absorption spectrometry, respectively, using their $H_2O_2$ solutions.

### *Spectroscopies*

Raman spectra were recorded using a JEOL JRS-400 spectrometer equipped with an Ar laser (514.5 nm). Infrared spectra were recorded for KBr pellet samples using a Nicolet MX-S Fourier transform-type spectrometer. High resolution (0.5 $cm^{-1}$) IR spectra were recorded using a DIGILAB FTS-20C spectrometer.

### *Monitoring Thermal Decomposition*

Thermogravimetric and differential thermal analyses were conducted using a ULVAC TA-1500 type TG/DTA thermal analyzer. A mass spectrometer (Hitachi M-70) was employed to monitor the gases generated during thermal decomposition of the sample.

## Results and Discussion

### *Chemical Composition of Acids and Salts*

The results of the chemical analyses are summarized in Table I. As mentioned above, two types of CW-HPA with different C/W molar ratios were synthesized. The compounds in which C/W = 0.083 (1 : 12) and 0.16 (1 : 16) are denoted as CW-HPA(I) and (II), respectively. The ratio of C/W in each CW-HPA acid is identical to that in the corresponding Ba salt. As a result, it is obvious that carbon in the present heteropolyanions is retained during salt formation. This situation is similar for Cs salt formation. On the other hand, a par-

TABLE I

RESULTS OF THE CHEMICAL ANALYSIS FOR CW-HPA'S, W-IPA, AND THEIR SALTS (IN MOLAR RATIO)

| | | CW-HPA(I) | CW-HPA(II) | W-IPA |
|---|---|---|---|---|
| Acids | $H^+/W$[a] | 0.72 | ~0.8 | 0.84 |
| | C/W | 0.083 | 0.16 | (~0.01) |
| | O–O/W | 0.58 | 0.55 | 0.57 |
| Ba salts | Ba/W | 0.28 | 0.31 | 0.27 |
| | C/W | 0.083 | 0.16 | (~0.01) |
| | O–O/W | 0.28 | 0.30 | 0.25 |
| Cs salts | Cs/W | ~0.5 | Not available | ~0.5 |
| | C/W | 0.083 | | (~0.01) |
| | O–O/W | 0.22 | | 0.2 |

[a] $H^+$ released when the Ba salts are formed.

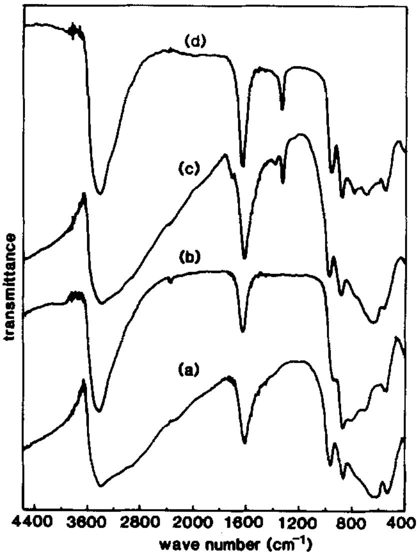

FIG. 2. Infrared spectra of W-IPA and CW-HPA(II) and their Ba salts: (a) W-IPA, (b) Ba · W-IPA, (c) CW-HPA, and (d) Ba · CW-HPA. The strong bands around 3400 and 1620 cm$^{-1}$ are due to $H_2O$ in solid state.

tial loss in the peroxo(O–O) groups takes place during the salt formation. Therefore, the hetero (or iso) polyanions in the salts may not be exactly the same as those in the initial acids.

### *Infrared and Raman Spectra of the Acids and Their Salts*

The infrared spectra of CW-HPA(II), W-IPA, and their Ba salts are shown in Fig. 2. The absorption bands at 1340 and 1400 cm$^{-1}$(weak) observed with CW-HPA(II) (Fig. 2c) may be assigned to $\nu_3$ of the $CO_3$ group. Inorganic carbonates such as $BaCO_3$ usually have the $\nu_3$ band around the 1400–1500 cm$^{-1}$ region (*6*). The corresponding bands are missing in the spectrum of the carbon-free W-IPA, but the remaining parts of these two spectra are similar. CW-HPA(I) showed a similar IR spectrum in Fig. 2c, but the bands at 1340–1400 cm$^{-1}$ were weaker, confirming that its carbon content is about half of that in CW-HPA(II). Each Ba salt gives a spectrum similar to its corresponding acid, as shown in Figs. 2b and 2d. An exception to this is that the band at 980 cm$^{-1}$ (probably due to W=O stretching plus $\nu_1(CO_3)$) is lowered to 950 cm$^{-1}$.

The Raman spectra of a CW-HPA(II) solution and its salt (solid state) are shown in Fig. 3. The band at 880 cm$^{-1}$ may be assigned to peroxo(O–O) stretching (*7*). The spectroscopic data shown above suggest that the anion structure remains almost unchanged whether in solution, solid acid, or barium salt. Other salts (Rb, Cs, or Pb · CW-HPA (or W-IPA)) showed basically the same Raman as well as IR spectra. The only exception is Ag · CW-HPA (or W-IPA), the Raman spectrum of which lacks a band at 880 cm$^{-1}$. Therefore, it is likely that the O–O groups in the anion of the original acid are totally removed when the Ag salt is formed.

### *Thermal Decomposition of Ba Salts*

The results of the thermogravimetric/differential thermal analysis (TG/DTA) recorded with Ba · W-IPA and Ba · CW-HPA are shown in Fig. 4. An intermediate stage in the temperature range from 300 to 520°C is seen in both TG curves. X-Ray

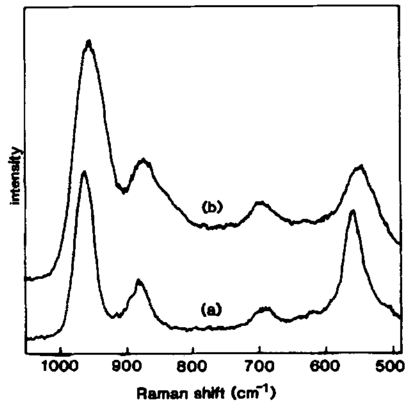

FIG. 3. Raman spectra of CW-HPA(II) and its barium salt: (a) CW-HPA, in solution; (b) Ba · CW-HPA, solid state.

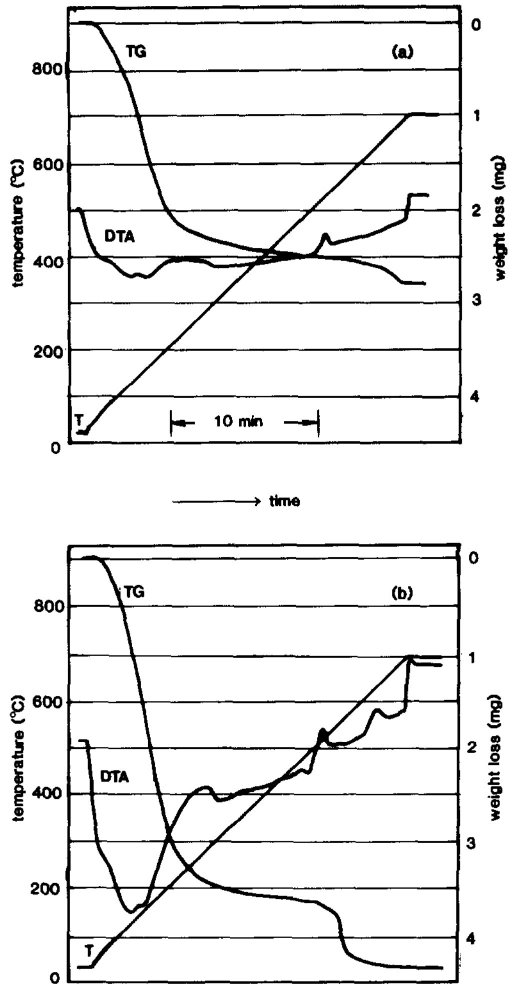

FIG. 4. Results of thermogravimetric (TG) and differential thermal (DT) analysis of (a) Ba · W-IPA and (b) Ba · CW-HPA. Initial weights: 21.1 mg and 28.2 mg, respectively. Heating rate (T) = 30°C/min. Atmosphere: dry air (30 ml/min).

diffractions showed that an amorphous phase in the intermediate stage starts to crystallize at 520°C, resulting in an unreported phase Y (Fig. 5a). Phase Y was then transformed into another unreported one, Phase X (plus trace of $BaWO_4$, Fig. 5b) at 600–700°C. This phase was finally disproportionated into triclinic $WO_3$ and $BaWO_4$ at higher temperatures (800–900°C, Fig. 5c).

Gas emissions released during such a thermal decomposition process were monitored using apparatus equipped with a mass spectrometer (MS). Sample (Ba · CW-HPA or Ba · W-IPA) powder was heated stepwise from $T_1$ to $T_2$ and maintained at $T_2$ for 15 min. The gas emitted during this step was allowed to fill the apparatus having a volume of 760 ml (the volume of a reaction tube installed into a furnace was only several milliliters) and was then introduced into the MS at the end of each step. The results are summarized in Table II. They reveal that: (i) almost all the carbon in Ba · CW-HPA is released as $CO_2$ in temperature regions higher than 500°C; (ii) the emission of $O_2$ (of peroxo origin) from this compound has two maxima, 100–200°C and 500–600°C; and (iii) in contrast to Ba · CW-HPA, Ba · W-IPA releases substantially all of its oxygen at temperatures between 500 and 600°C.

The infrared spectra of Ba · CW-HPA(II) heated at various temperatures (200–700°C)

TABLE II

MASS-SPECTROSCOPICALLY DETERMINED $CO_2$ AND $O_2$ EMISSION FROM BA SALTS DURING THEIR THERMAL DECOMPOSITION (IN $\mu$mole[a])

| Temperature range ($T_1$ ~ $T_2$°C)[d] | Ba · CW-HPA(II)[b] $CO_2$ | Ba · CW-HPA(II)[b] $O_2$ | Ba · W-IPA[c] $O_2$ |
|---|---|---|---|
| rt ~ 100 | 0.0(---) | 0.03(---) | 0.04(---) |
| 100 ~ 200 | 0.02(0.02)[e] | 0.45(0.48) | 0.16(0.20) |
| 200 ~ 300 | 0.08(0.10) | 0.28(0.76) | 0.02(0.22) |
| 300 ~ 400 | 0.29(0.39) | 0.21(0.97) | 0.01(0.23) |
| 400 ~ 500 | 0.39(0.78) | 0.14(1.11) | 0.01(0.24) |
| 500 ~ 600 | 1.75(2.53) | 0.35(1.46) | 1.99(2.23) |
| 600 ~ 700 | 0.01(2.54) | 0.00(1.46) | 0.00(2.23) |

[a] Calculated from the volume of the apparatus and MS signals calibrated against pressures.

[b] Sample weight 4.1 mg, containing 12.2 $\mu$mol of W.

[c] Sample weight 4.1 mg, containing 13.1 $\mu$mol of W.

[d] In each step, samples were heated from $T_1$ to $T_2$ in about 2 min and kept at $T_2$ for 15 min.

[e] Figures in parentheses are the accumulated emission from rt to $T_2$.

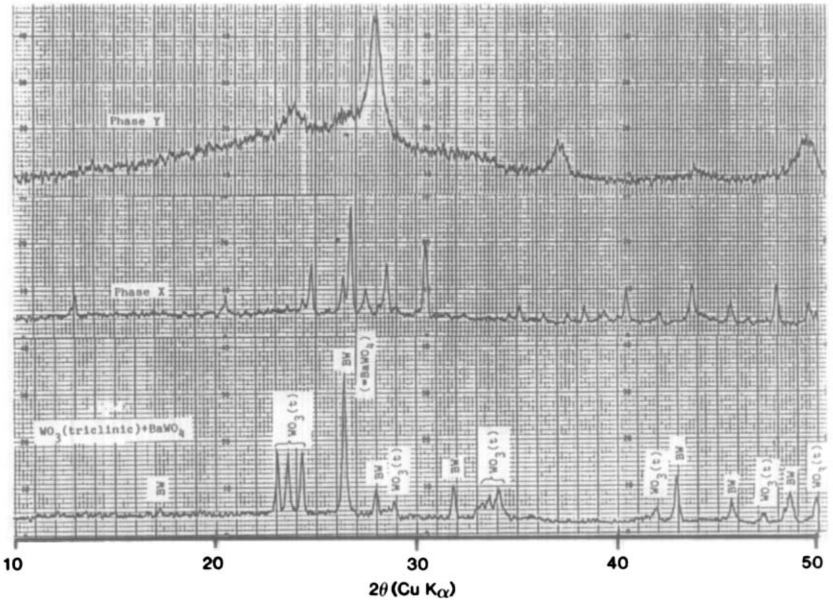

FIG. 5. Powder X-ray diffraction profiles of crystalline phases derived from Ba · CW-HPA during its thermal decomposition. Phase Y: 520°C-heated Ba · CW-HPA. Phase X: 700°C. $WO_3$ + $BaWO_4$ mixture phase: 900°C.

for 20–30 min in air were recorded at room temperature. The results, with the gas chromatographically determined C/W ratios for each sample, are shown in Fig. 6. These spectra clearly show that with increasing heat treatment temperature, the bands due to $\nu_3$ ($CO_3$) at 1340–1400 $cm^{-1}$ decrease. At the same time, a new band at 2340 $cm^{-1}$ increases with temperatures up to 400°C. This band is due to $\nu_2$ vibration of $CO_2$. The usually accepted frequency is 2349 $cm^{-1}$ (gas phase). Throughout this process, no significant change in the C/W ratio takes place. It is therefore obvious that the $CO_2$ resulting from the decomposition of the heteropolyanion is retained in the compound. Decomposition probably starts near 200°C, where a weak and vague endothermic peak is seen in DTA. Referring to both the mass spectroscopy (Table II) and the DTA (Fig. 4b) results, such caged $CO_2$ is rapidly released at the crystallization temperature (about 520°C). Consequently, no bands are seen around 2340 $cm^{-1}$ for the sample treated at 700°C.

Similar TG/DTA decomposition curves are given by Ba · W-IPA, as shown in Fig. 4a. In this case, however, the final weight loss at temperatures around 500°C is solely due to the release of $O_2$. For Ba · CW-HPA, on the other hand, the final weight loss results from the release of either $O_2$ or $CO_2$, as seen from Table II. In addition, there was no band around 2340 $cm^{-1}$ in the IR spectrum of the heat-treated Ba · W-IPA.

Almost the same thermal decomposition behavior noted above was observed for the Pb or Ag salt of CW-HPA or W-IPA. The caging phenomenon of $CO_2$ (and/or $O_2$) was also seen in an intermediate phase during thermal decomposition. However, neither $CO_2$ nor $O_2$ was caged for the Cs or Rb salts which decomposed in one step or, in other

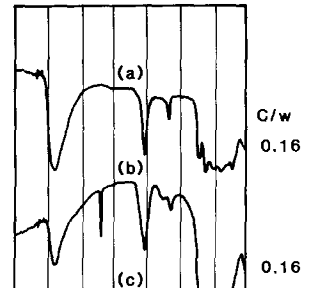

FIG. 6. Infrared spectra of Ba · CW-HPA heat-treated at various temperatures (recorded at room temperature using the KBr pellet technique). Gas chromatographically determined C/W molar ratios are shown outside the spectra. (a) 50°C (as-prepared sample); (b) 200°C, 30 min; (c) 320°C, 30 min; (d) 400°C, 25 min; (e) 520°C, 20 min; (f) 700°C, 20 min. Bands at 1340–1400 cm$^{-1}$ are due to $CO_3$ which decrease with increasing treatment temperatures, while a band at 2340 cm$^{-1}$ is due to $CO_2$ which increases up to 400°C.

words, had no intermediate stage during decomposition.

### *Raman and High-Resolution IR Spectra of Heat-Treated Ba Salts*

The Raman spectra of 400°C-treated Ba · CWHPA and Ba · W-IPA are shown in Fig. 7. Here, thin green pellets were used for measurements. In the spectrum of Ba · CW-HPA (Fig. 7a), the $\nu_1$ vibration of $CO_2$ (splitting due to the Fermi resonance) is seen around 1380 and 1270–1280 cm$^{-1}$. This vibration is Raman active only and its usually accepted frequencies are 1388 and 1286 cm$^{-1}$. A higher resolution recording revealed that the $CO_2$ peak at around 1380 cm$^{-1}$ was quite broad and asymmetric. In addition to the $CO_2$ peaks, a band obviously due to the $O_2$ vibration is observed at 1553 cm$^{-1}$ in Fig. 7a. The usually accepted vibrational frequency of $O_2$ (gas) is 1555 cm$^{-1}$. On the other hand, only an oxygen peak is observed in the spectrum of Ba · W-IPA at the same wave number (Fig. 7b).

A high-resolution (0.5 cm$^{-1}$) IR spectrum of 400°C-treated Ba · CW-HPA recorded between 2200 and 2500 cm$^{-1}$ is shown in Fig. 8a. For comparison, a spectrum of gas phase $CO_2$ (atmospheric) is given in Fig. 8b. In the latter figure, a fine structure of the antisymmetric $\nu_2$ due to molecular rotation can be clearly seen. However, the strong band in Fig. 8a due to the corresponding vibration of $CO_2$ does not have a fine structure (the very weak band at 2280 cm$^{-1}$ is not yet assigned). Consequently, it is obvious that the $CO_2$ in the heat-treated Ba · CW-HPA lacks freedom of rotation, and this is probably due to interaction with its surroundings. Such a $CO_2$ cannot be in a state of surface adsorption but is caged instead in an amorphous network structure of barium tungsten oxide. This is because molecular adsorption is unlikely at such high temperatures, and because the C/W ratio in the initial Ba · CW-HPA (as $CO_3$) is essentially identical with that in the corresponding phase up to 400°C. In addition, it should be noted that $CO_2$ is not in a gaseous state encapsulated in microvoids, but each $CO_2$ molecule is so closely surrounded by the amorphous network that its rotation is prohibited. The fact that the $\nu_1$ Raman band profile of $CO_2$ is broad and asymmetric can also be interpreted assuming the above $CO_2$ condition.

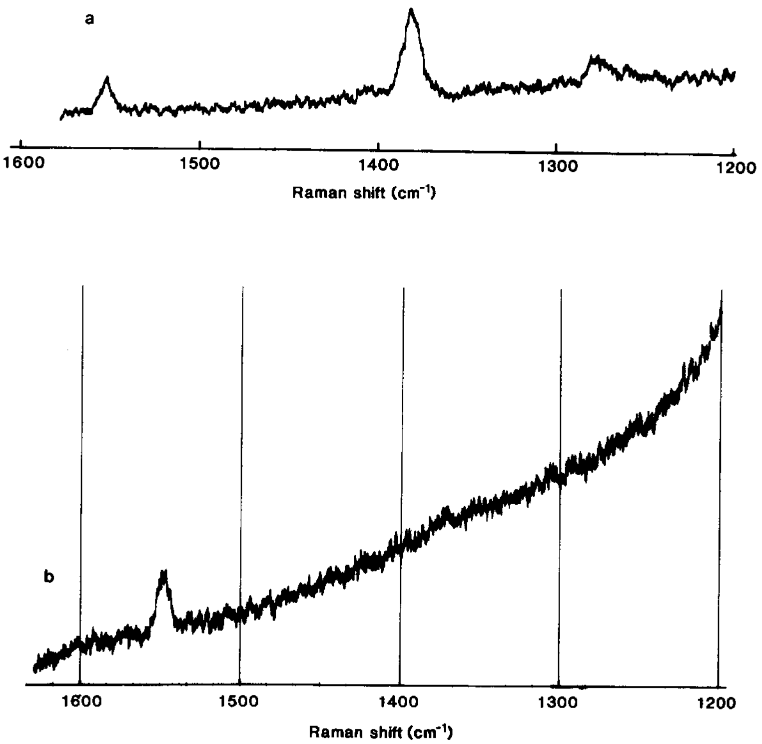

FIG. 7. Raman spectra of 400°C-treated (a) Ba · CW-HPA and (b) Ba · W-IPA (recorded at room temperature). The bands at 1280 and 1380 cm$^{-1}$ seen in (a) are due to the symmetric vibration of $CO_2$ in the sample. A band at around 1550 cm$^{-1}$, seen in both (a) and (b), is due to $O_2$ in the samples.

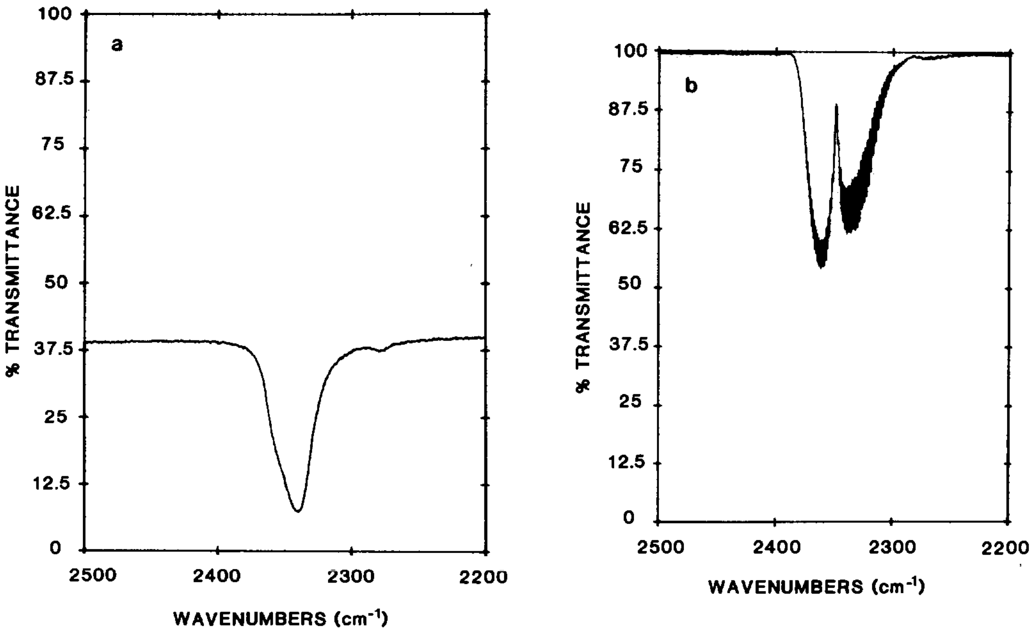

FIG. 8. Infrared spectra of the antisymmetric $\nu_2$ vibration of $CO_2$ molecules: (a) $CO_2$ in 400°C-treated Ba · CW-HPA and (b) atmospheric $CO_2$. A fine structure due to molecular rotation seen in (b) is missing in (a).

### *Empirical Formula of Barium Tungsten Oxides Caging $CO_2$ and/or $O_2$*

The weight loss of Ba · CW-HPA(II) observed by TGA (Fig. 4b) between 400 and 700°C corresponds to the loss of $2CO_2 + \frac{1}{2}O_2$ per 12 mole W. This generally agrees with results from the mass spectroscopic gas analysis (Table II). Since Ba/W = 0.31 ($\doteqdot \frac{1}{3}$), the intermediate phase (a kind of $CO_2$ and $O_2$ complex) can be expressed by the empirical formula

$$4BaO \cdot 12WO_3 \cdot \tfrac{1}{2}O_2^* \cdot 2CO_2^* \qquad (A)$$

where $O_2^*$ and $CO_2^*$ represent oxygen and carbon dioxide molecules caged in the compound. From TGA and other analyses, the thermal decomposition of Ba · CW-HPA can be described as

$$\begin{array}{l} 4BaO \cdot 12WO_3 \cdot 4H_2O_2 \cdot 2CO_2 \cdot 18H_2O \\ \qquad\big\downarrow \text{ rt—200°C, } -(3H_2O_2 + 18H_2O) \\ 4BaO \cdot 12WO_3 \cdot H_2O_2 \cdot 2CO_2 \\ \qquad\big\downarrow \text{ 200—400°C, } -H_2O \\ \qquad[A] \\ \qquad\big\downarrow \text{ 400—700°C, } -(\tfrac{1}{2}O_2 + 2CO_2) \\ \quad 4BaO \cdot 12WO_3. \end{array}$$

Similarly, the intermediate phase of Ba · W-IPA can be expressed by the empirical formula

$$3BaO \cdot 12WO_3 \cdot \tfrac{3}{2}O_2. \qquad (B)$$

This is derived from the room temperature Ba · W-IPA with an empirical formula

$$3BaO \cdot 12WO_3 \cdot 3H_2O_2 \cdot 16H_2O. \quad (C)$$

In the amorphous phases (A) or (B), it is very likely that $CO_2$ and/or $O_2$ molecules are closely surrounded by $WO_6$ octahedra, which, as a whole, construct a random network. A similar inclusion phenomenon for Ne in sputtered amorphous silicon has recently been discovered by XPS studies, although Ne is introduced during the sputter process in this case (*8*).

### *$CO_2/H_2O$ Exchange Phenomenon in Compound (A)*

Caged $CO_2$ is so stable that it cannot be eliminated by evacuation. For example, changes in the C/W ratio were not observed when 333°C-treated Ba · CW-HPA(II) was reheated at the same temperature under a $10^{-5}$ torr vacuum for 30 min. However, it was found that $CO_2$ in 333°C-treated Ba · CW-HPA was almost completely lost after storage for 1 month in a normal atmosphere at room temperature. The higher the humidity, the faster the $CO_2$ loss.

The $H_2O$/W ratio in the sample which had lost $CO_2$ was about 1.0, which is much larger than the value 0.07 obtained with the sample still retaining $CO_2$ (i.e., immediately after the heat treatment). It is therefore clear that $CO_2$ caged in Ba salt is replaced by $H_2O$. It was confirmed that this $CO_2/H_2O$ exchange process is irreversible.

Although the same exchange phenomenon was also seen for the Ag salt, the exchange rate was much slower than that in the Ba salt. For Pb · CW-HPA, however, no exchange was observed after storage for 1 month at room temperature with a saturated humidity. The dependence of $CO_2$ caging and the $CO_2/H_2O$ exchange phenomena on the cation is summarized in Table III.

TABLE III

CATION DEPENDENCE OF $CO_2$ CAGING PHENOMENON IN *M* · CW-HPA

| | Cation (*M*) | | | | |
|---|---|---|---|---|---|
| | $Cs^+$ | $Rb^+$ | $Ba^{2+}$ | $Pb^{2+}$ | $Ag^+$ |
| $CO_2$ caging | No | No | Yes | Yes | Yes |
| $CO_2/H_2O$ exchange rate | — | — | Fast | Very slow | Slow |

## Conclusion

We have investigated several inorganic salts derived from a recently found tungsten-based hetero(carbon)polytungsticacid and its *iso*-version.

It has been found that $CO_2$ resulting from heteroatoms in the polyanion is almost totally caged in an amorphous intermediate phase of a thermal decomposition process of a Ba salt derived from the heteropolyacid. In addition, this amorphous phase cages $O_2$ and may be expressed by the formula

$$4BaO \cdot 12WO_3 \cdot \tfrac{1}{2}O_2 \cdot 2CO_2.$$

The caged $CO_2$ and $O_2$ are released at the crystallization temperature (520°C). The infrared active $\nu_2$ vibration of such $CO_2$ lacks a fine structure due to its rotation. Furthermore, the salts with Pb and Ag show a similar caging phenomenon, but those with Rb and Cs do not.

This study presents the first demonstration of $CO_2$ as well as $O_2$ molecules caged in a solid framework at a definite stoichiometric ratio.

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