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Absorption effects of carbon tetrachloride on the structural and thermodynamic properties of copper(II) *trans*-1,4-cyclohexanedicarboxylate

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Abstract

Large amount of carbon tetrachloride can be absorbed into 1-dimensional tunnels in copper(II) *trans*-1,4-cyclohexane dicarboxylate (Cu(*trans*-1,4-$OOCC_6H_{10}COO$)) under the saturated vapor pressure at room temperature, and the desorption can be performed easily by evacuation above room temperature. It has been confirmed that the absorption/desorption is reversible. The thermodynamic and structural properties were studied for the empty (non-absorbed) sample, and 10, 22 and 31% of full carbon tetrachloride-absorbed samples by adiabatic calorimetry between 13 and 300 K and by powder X-ray diffractometry with high-energy synchrotron radiation at SPring-8 of JASRI. The heat capacity anomaly due to the first-order phase transition observed in the empty sample was not observed in the full carbon tetrachloride-absorbed sample. However, the partially absorbed samples showed smaller heat capacity anomaly at lower temperatures than the empty sample. Such phenomena were compared with the previous results of toluene-absorbed sample, and the difference between the two cases was discussed.

Keywords: Copper(II) *trans*-1,4-cyclohexanedicarboxylate (Cu(*trans*-1,4-$OOCC_6H_{10}COO$)); Heat capacity; Powder X-ray diffraction; Phase transition; Carbon tetrachloride

1. Introduction

Microporous materials for the use of absorption/desorption of large amount of molecules have attracted increasing attention in the fields of basic science and various applications. This arises from the advent of thermally stable and robust open infinite one-, two- and three- dimensional frameworks in the absence of guest molecules [1–9]. While much effort has been paid to search for such new microporous metal–organic materials, little attention has been paid to the structure and motion of guest molecules absorbed in the pores.

The present authors have recently studied thermodynamic properties of copper(II) *trans*-1,4-cyclohexane dicarboxylate (Cu(*trans*-1,4-$OOCC_6H_{10}COO$); abbreviated as Cuchd), which can absorb and desorb large amount of benzene and toluene [10]. A first-order phase transition has been found at 160 K for the empty (non-absorbed) sample of Cuchd, which was detected as an anomaly in the curves of heat capacity and of magnetic susceptibility. The crystal structure is shown schematically in Fig. 1. The structural change due to the phase transition was confirmed by X-ray crystallography [11]. On the other hand, a small anomaly due to the phase transition was observed for partially toluene-absorbed sample, and the experimental results were compared and discussed in the previous studies [10–12]. Thus the present authors extended the studies to absorption/desorption of carbon tetrachloride in Cuchd. From the calorimetry for heat capacity measurements and powder X-ray diffractiometry with high-energy synchrotron radiation SPring-8, it was found that absorbed carbon tetrachloride should interact with the host lattice by a different mechanism from that of toluene-absorbed sample.

2. Experimental

2.1. Sample preparation

The sample of Cuchd was synthesized in methanol solution as follows [13]. Methanol (Wako Pure Chemicals; 99.9% purity, 600 cm^3) solution of copper(II) formate (Wako P.C.; 98%, 4.06 g) was added to another methanol solution (300 cm^3) of

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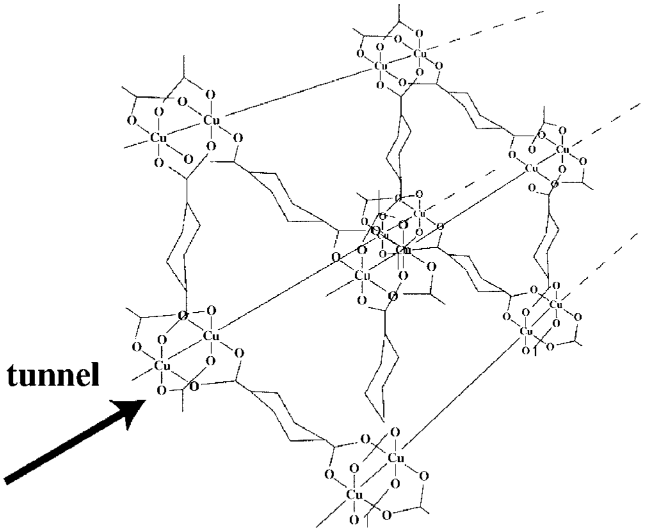

Fig. 1. Structure of Cu(*trans*-1,4-OOCC_6H_{10}COO) (Cuchd).

trans-1,4-cyclohexane dicarboxylic acid (Wako P.C.; 99.9%, 3.1 g) and of formic acid (Wako P.C.; 99%, 60 cm^3). The mixture was put in a sealed flask, which was allowed to stand for several weeks at room temperature. Thus greenish blue fine crystals precipitated in the solution, and were separated by filtering. The specimen was heated at 100 °C for 4 h in vacuum to remove the solvent. Chemical analysis for the elements of C, H and O gave good agreement with the calculated values, which indicated that the sample was successfully synthesized.

2.2. Heat capacity measurements

The heat capacity measurements were made using a home made adiabatic calorimeter between 13 and 300 K. The working thermometer mounted on the calorimeter vessel (gold plated copper) was an iron–rhodium resistance thermometer (model 5187U, Tinsley and Co. Ltd., U.K.) calibrated on the basis of ITS-90 at National Physical Laboratory and at Oxford Instruments Ltd., U.K. A small amount of helium gas (6 kPa at room temperature) was introduced in the calorimeter vessel to improve the thermal uniformity. The details of the apparatus and the operation have been described previously [14,15]. The empty sample of 3.654 g (0.0156 mol) was put in the calorimeter vessel, evacuated in a vacuum and then exposed under the saturated vapor of carbon tetrachloride at room temperature. By measuring the weight, the amount of the absorbed carbon tetrachloride was determined as 0.400, 0.280 and 0.130 g, which was about 10, 22 and 31% of that of the full absorption, respectively.

2.3. Powder X-ray diffraction

The powder X-ray diffractiometry with synchrotron radiation ($\lambda = 0.8007$ Å) was performed at the BL02B2 in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). The range of reflection angle was $5^\circ < 2\theta < 80^\circ$. The sample was put in a Pyrex glass capillary (0.3 mm in inside diameter, 2 cm in length), and the capillary was connected to the Pyrex glass vacuum line. After evacuation, the sample was exposed under the saturated vapor of carbon tetrachloride at room temperature to absorb full amount of carbon tetrachloride, and then it was sealed off by a hand torch.

3. Results and discussion

The heat capacity measurements were carried out between 30 and 300 K for 10, 22 and 31% carbon tetrachloride-absorbed Cuchd samples. The heat capacity could not be measured below 30 K, because the helium gas put inside the calorimeter vessel for heat exchange was absorbed into the sample and thus the time to attain the thermal equilibrium after each heat input was extremely long. The measured molar heat capacities of without curvature corrections are shown in Fig. 2 together with the previous data of the empty Cuchd [10].

It is clearly seen that the partially carbon tetrachloride-absorbed samples showed a smaller anomaly at lower temperature than that of the empty sample. The excess heat capacity due to the first order phase transition of 10, 22 and 31% carbon tetrachloride-absorbed Cuchd was calculated by subtracting the normal base line from the measured molar heat capacity. The separated excess heat capacity is shown in Fig. 3 together with those of the 11 and 21% toluene-absorbed samples [10]. By integrating the excess heat capacity, the enthalpy of transition was determined as 233, 128 and 37 J mol^{-1} for 10, 22 and 31% carbon tetrachloride-absorbed samples, respectively. The numerical values of thermodynamic properties of the phase transition calculated from the results of calorimetry are given in

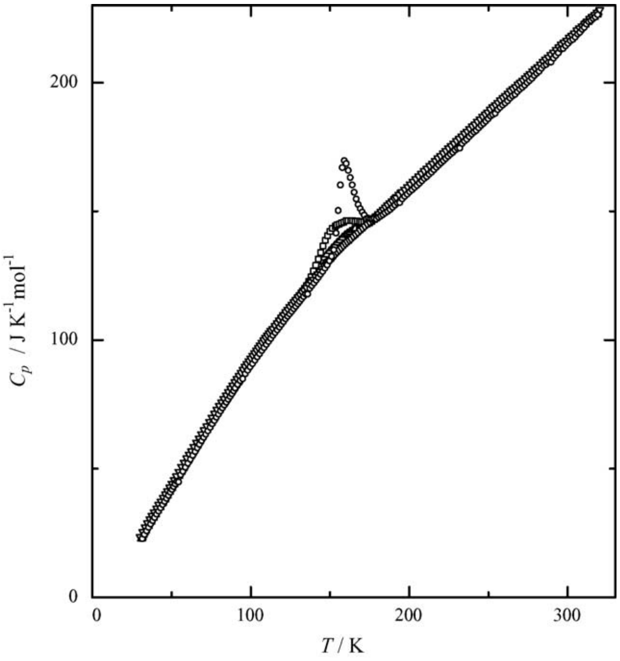

Fig. 2. Measured molar heat capacity of empty Cuchd (circle), 10% carbon tetrachloride-absorbed Cuchd (square), 22% carbon tetrachloride-absorbed Cuchd (triangle) and 31% carbon tetrachloride-absorbed Cuchd (inverted triangle).

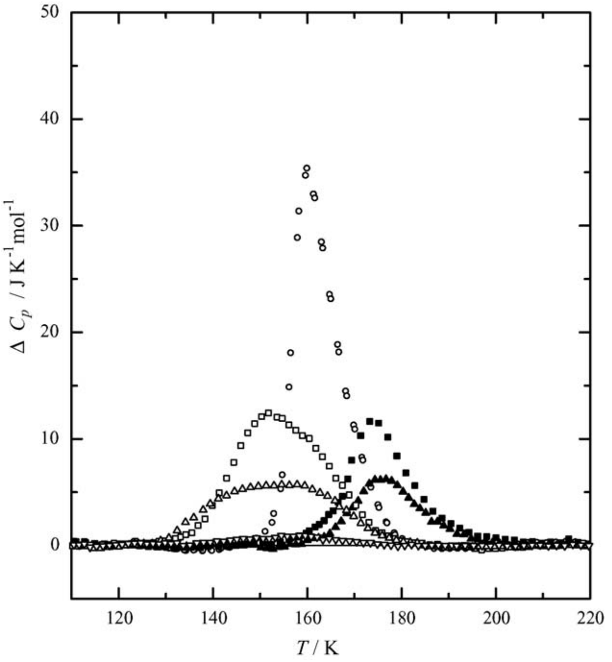

Fig. 3. Excess heat capacity due to the phase transition of empty Cuchd (circle), 31% carbon tetrachloride-absorbed Cuchd (inverted triangle), 22% carbon tetrachloride-absorbed Cuchd (triangle), 10% carbon tetrachloride-absorbed Cuchd (square), 21% toluene-absorbed Cuchd (closed triangle) and 11% toluene-absorbed Cuchd (closed square).

Table 1. It is very interesting that the enthalpy of transition of the 10% carbon tetrachloride-absorbed sample was 56% of that of the empty sample. Thus the absorbed carbon tetrachloride influences greatly this phase transition, which is very similar to toluene-absorbed sample. However, the transition temperature is shifted to lower temperatures by absorbing carbon tetrachloride, while it shifts to higher temperatures in the case of toluene-absorption samples [10].

The powder X-ray diffractometry with synchrotron radiation ($\lambda = 0.8007$ Å) was performed fully and 10% carbon tetrachloride-absorbed samples at temperatures from 100 to 300 K. The results are shown in Figs. 4 and 5 together with the previous data of empty Cuchd [11]. According to the first order phase transition at 160 K, significant structural difference is clearly seen between the low temperature phase and the high temperature phase [11]. In the case of fully toluene-absorbed sample, no phase transition was observed and the structure is similar to that of the low temperature phase of empty Cuchd in whole temperature region [11]. On the hand, the diffraction pattern of fully carbon tetrachloride-absorbed Cuchd at 300 K is similar to that of the high temperature phase of the empty sample. Below 250 K, the diffraction pattern of fully carbon tetrachloride-absorbed sample was essentially similar to that at 300 K, but some new peaks (denoted with arrows in Fig. 5) appeared below 250 K. These new peaks cannot be related with the original peaks but correspond to the low temperature phase of the empty samples. It indicates that fully carbon tetrachloride-absorbed Cuchd separate into two phases below 250 K. The 10% carbon tetrachloride-absorbed sample has the similar diffraction patterns as empty sample at 300 K, which indicates that the structure is that of the high temperature phase of the empty sample. The diffraction patterns drastically changed between 300 and 150 K due to the phase transition. However, peaks of high temperature phase remained slightly in 10% carbon tetrachloride-absorbed sample even at 100 K. Thus, the partly carbon tetrachloride-absorbed samples have two phases at low temperature, which is similar to fully absorbed sample.

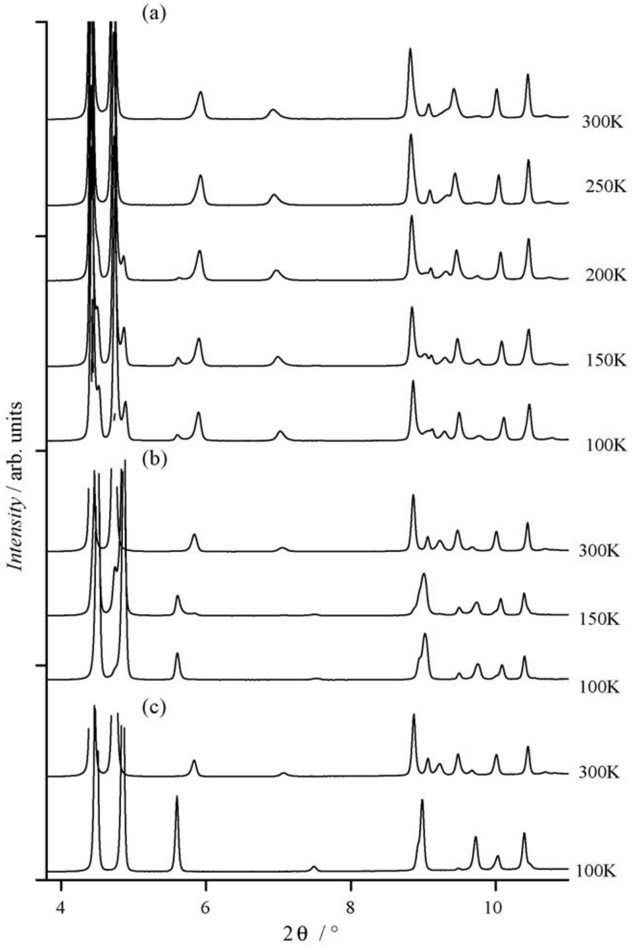

Fig. 4. Powder X-ray diffraction patterns of Cuchd. (a) Fully carbon tetrachloride-absorbed; (b) 10% carbon tetrachloride-absorbed; (c) empty sample.

Table 1
Thermodynamic properties of the phase transition in copper(II) *trans*-1,4-cyclohexanedicarboxylate and those of carbon tetrachloride-absorbed and toluene-absorbed samples

Samples	T_{trs} (K)	$\Delta_{\mathrm{trs}}H$ (J mol^{-1})	$\Delta_{\mathrm{trs}}S$ (J K^{-1} mol^{-1})
Empty	160	413.4	2.66
31% carbon tetrachloride	151	36.7	0.25
22% carbon tetrachloride	151	127.5	0.77
10% carbon tetrachloride	151	232.5	1.53
65% toluene	–	–	-
21% toluene	177	119.7	0.64
11% toluene	174	208.1	1.25

T_{trs}, transition temperature; $\Delta_{\mathrm{trs}}H$, enthalpy of transition; $\Delta_{\mathrm{trs}}S$, entropy of transition.

Table 2
Lattice constants of empty, fully toluene-absorbed and fully carbon tetrachloride-absorbed Cuchd at 100 and 300 K

Samples	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
Empty (100 K)	11.0	9.98	4.70	99.01	106.32	103.16	472.78
Empty (300 K)	10.55	9.89	5.07	86.26	93.19	100.95	517.74
Toluene-absorbed (100 K)	10.98	9.97	4.69	99.65	104.65	103.16	468.23
Toluene-absorbed (300 K)	10.98	9.96	4.72	97.94	103.32	104.44	476.12
Carbon tetrachloride-absorbed (100 K)	10.62	9.87	5.16	85.54	99.49	99.79	524.17
Carbon tetrachloride-absorbed (300 K)	10.77	9.98	5.16	85.54	99.49	99.69	538.87

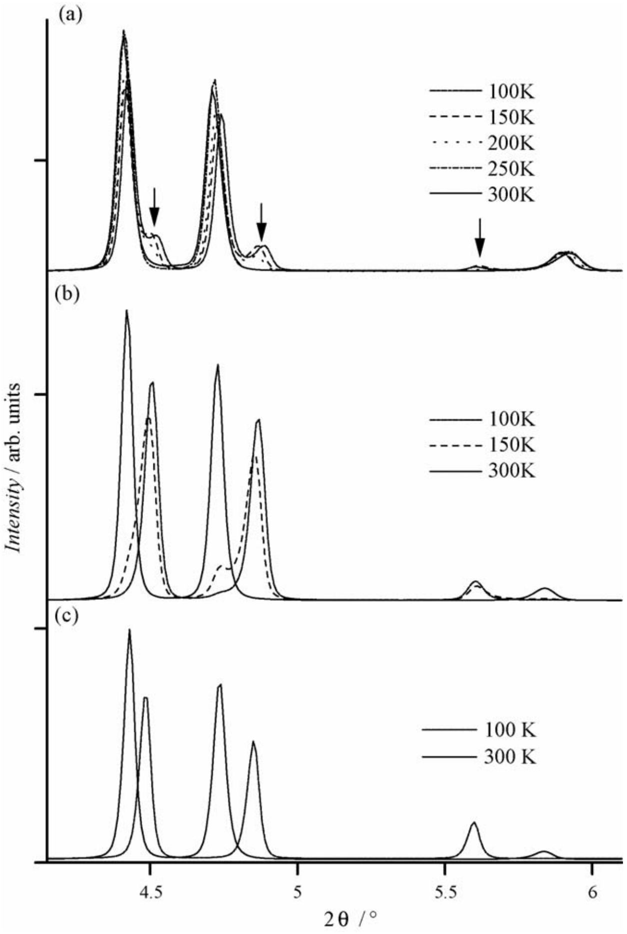

Fig. 5. Low angle powder X-ray diffraction patterns of Cuchd. (a) Fully carbon tetrachloride-absorbed; (b) 10% carbon tetrachloride-absorbed; (c) empty sample.

In the case of the fully toluene-absorbed Cuchd, the structure is of the low temperature phase of empty Cuchd in whole temperature region. Such opposite change should be caused by the different interaction between the guest molecules and the host lattice. The lattice parameters and cell volumes of fully carbon tetrachloride-absorbed Cuchd at 100 and 300 K were determined using the indexing program *TREOR*90 [16], and the results are given in Table 2 together with the data of empty and toluene-absorbed Cuchd [11]. The lattice parameter at 100 K of carbon tetrachloride-absorbed Cuchd was calculated for the main phase. The crystal cell volume expands with absorbing carbon tetrachloride, contrary to the constriction with absorbing toluene. This indicates the difference of guest–host interaction between the cases of carbon tetrachloride-absorbed and toluene-absorbed Cuchd. The further studies to investigate the interaction of various guest molecules with the host lattice are in progress.

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