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Thermal studies of copper(II) fumarate and copper(II) terephthalate

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Abstract

Copper(II) fumarate ($Cu(OOCC_2H_2COO)$) and copper(II) terephthalate ($Cu(OOCC_6H_4COO)$) have been synthesized. Their heat capacity has been measured by adiabatic calorimetry between 13 and 300 K and their magnetic susceptibility determined with a SQUID magnetometer between 5 and 300 K. No phase transition has been observed in the whole temperature range covered by the experiments. The thermodynamic properties of these compounds are compared with those of copper(II) *trans*-1,4-cyclohexane dicarboxylate, in which a structural first-order phase transition was observed at 160 K.

Keywords: Heat capacity; Magnetic susceptibility; Copper(II) fumarate ($Cu(OOCC_2H_2COO)$); Copper(II) terephthalate ($Cu(OOCC_6H_4COO)$)

1. Introduction

Highly functional microporous metal-organic frameworks have been found in a series of organometallic compounds constructed by co-polymerization of organic groups and metal ions. They have been receiving widespread attention in recent years because of their reversible absorption/desorption of great variety and large amount of molecules. The bridging group within the framework can be replaced with various substituent groups, and a number of functional compounds have been successfully synthesized [1–5]. For metal-organic frameworks, the central metal ions are linked by singly, doubly, or triply coordinated ligands, such as diamines, di-, or tri-carboxylate [6–8].

The present authors have studied thermodynamic properties of copper(II) *trans*-1,4-cyclohexane dicarboxylate (Cuchd), which can reversibly absorb/desorb large amount of benzene, toluene, and carbon tetrachloride [9]. A structural first-order phase transition has been found at 160 K for the empty (not-absorbed) sample of Cuchd, which was detected as an anomaly in the heat capacity and in the magnetic susceptibility. The structural change was confirmed by X-ray crystallography [10]. On the other hand, the fully absorbed sample of Cuchd has no phase transition. Recently, we extended our thermodynamic studies to other compounds of this family of compounds, copper(II) fumarate ($Cu(OOCC_2H_2COO)$; Cufud) and copper(II) terephtalate ($Cu(OOCC_6H_4COO)$; Cuted); their structures are shown schematically in Figs. 1 and 2, respectively. The samples of Cufud and Cuted have been synthesized and the heat capacity and the magnetic susceptibility measured at temperatures from liquid helium temperature to room temperature. The results are compared with those of previous studies on Cuchd [9,10].

2. Experimental

2.1. Sample preparation

The sample of $Cu(OOCC_2H_2COO)$ (Cufud) was synthesized in methanol solution as follows [11]. 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 fumaric 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 al-

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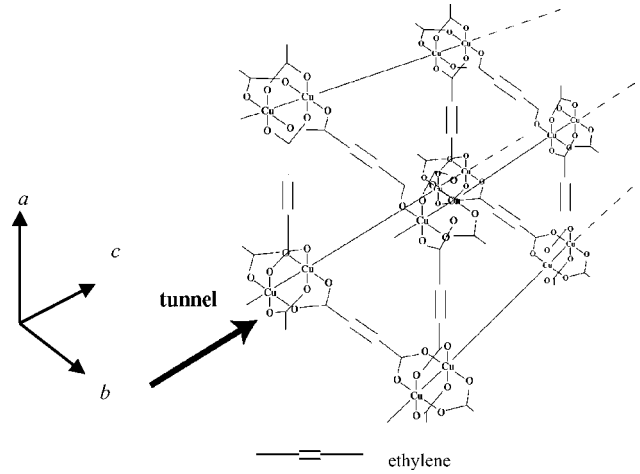

Fig. 1. Structure of $Cu(OOCC_2H_2COO)$ (Cufud).

lowed 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. The sample of Cuted was synthesized by the same method. Chemical analysis for the elements of C, H, and O gave good agreement with the calculated values, which showed that the synthesis was successful.

2.2. Heat capacity and magnetic susceptibility measurements

The heat capacity measurements were made using a homemade 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., UK) calibrated on the basis of ITS-90 at National Physical Laboratory and Oxford Instruments Ltd., UK. 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 [12,13]. The Cufud sample of 3.6546 g (0.02057 mol) was used for the heat capacity measurements. In the case of Cuted, the amount of the sample was 0.9796 g (0.004302 mol).

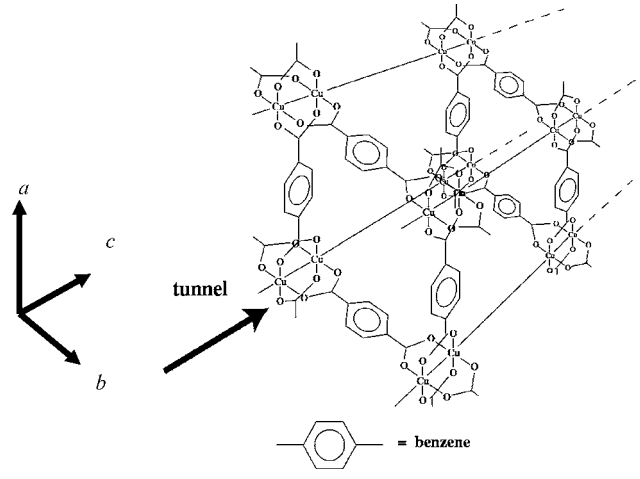

Fig. 2. Structure of $Cu(OOCC_6H_4COO)$ (Cuted).

For the magnetic measurements, the Cufud sample of 0.01102 g (0.06201 mmol) was put in a silica glass tube (2.5 mm in inside diameter). The glass tube was connected to a pyrex glass vacuum line, connected to a rotary pump equipped with liquid nitrogen trap. After evacuation, a small amount of helium gas (6 kPa at room temperature) was allowed inside the tube, and then the sample part was sealed off by a hand torch. The magnetic susceptibility was measured under a magnetic field of 1 T between 5 and 300 K using a SQUID magnetometer (MPMS, Quantum Design). For the measurements on Cuted, the amount of the sample was 0.01343 g (0.05898 mmol).

After the heat capacity measurements of the empty sample of Cufud, the sample was put in vacuum, and then it was exposed to benzene vapor saturated at room temperature. By weighing, the amount of the absorbed benzene was determined as 0.3090 g, which represented about 96% of full absorption.

3. Results and discussion

The calorimeter was cooled down to the liquid helium temperature and the adiabatic calorimetry was performed on heating direction. However, thermal equilibration within the calorimeter vessel was not attained rapidly enough in the lowest temperature region, as the samples of Cufud and Cuted absorbed the helium gas put inside the calorimeter vessel. Thus the heat capacity measurements could be made only above 30 K. The molar heat capacity of Cufud and Cuted obtained, without curvature corrections, are shown in Fig. 3 together with previous data for Cuchd [9]. As clearly seen in

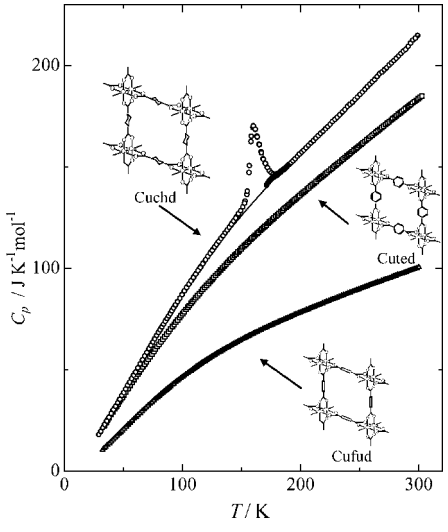

Fig. 3. Measured molar heat capacity of empty Cuchd (circle), Cufud (triangle) and Cuted (square).

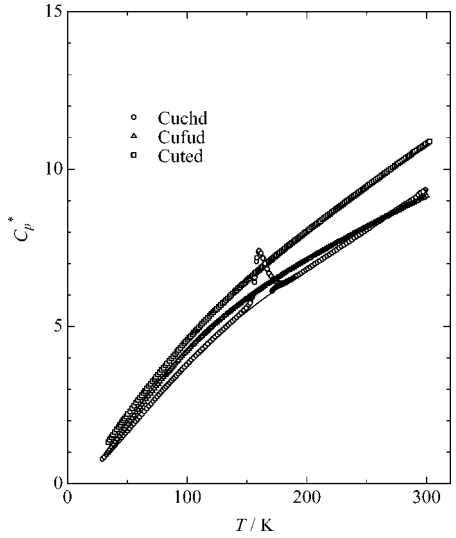

Fig. 4. Normalized heat capacity of Cuchd (circle), Cufud (triangle) and Cuted (square).

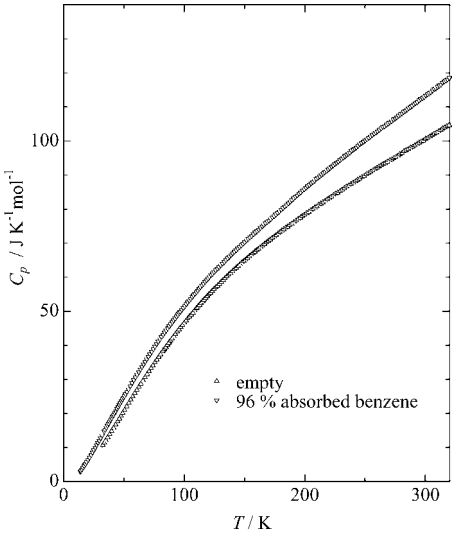

Fig. 5. Measured molar heat capacity of empty Cufud (triangle) and of 96% benzene absorbed Cufud (inverted triangle).

Fig. 3, no phase transition is observed in Cufud and Cuted, while Cuchd shows an anomaly at 160 K due to a structural phase transition [9,10]. No anomaly in Cufud and Cuted is also detected by the magnetic susceptibility measurements.

In Fig. 3, the molar heat capacity value of Cufud is extremely small as compared with Cuchd and Cuted. A probable reason may be the difference in the number of atoms in their chemical formulas. To see the intrinsic difference, the normalized molar heat capacity C_p^* is obtained by dividing C_p with the number of atoms, 11, 17 and 23, for Cufud, Cuted and Cuchd, respectively. The normalized heat capacity is shown in Fig. 4. At a glance, the heat capacity curves of Cufud and of Cuchd are very close to each other, while that of Cuted is higher. These results imply that the lattice vibrations of Cufud and Cuchd are very similar, and thus the force constants of their framework should be also very similar. On the other hand, the larger value of Cuted means that the framework of Cuted is less stiff as compared to Cufud and Cuchd.

It is also considered that the difference in molar heat capacity among these three compounds should be caused by the different contribution of the different substituted groups. For example, the heat capacity difference between Cuchd and Cuted (see Fig. 3) is attributed to the difference between the heat capacity of cyclohexane [14] and benzene [15].

To see the effect of absorption, the heat capacity measurements were made on the 96% benzene absorbed Cufud, and the results were compared with those of the empty sample of Cufud. In the case of benzene absorbed sample, the helium gas put in the calorimeter vessel was not absorbed into the sample of Cufud, and thus the heat capacity measurements could be made in the lowest temperature region. Both data sets are shown in Fig. 5, where the data for benzene absorbed sample could be obtained from the lowest temperature. The heat capacity values of the benzene absorbed sample are larger than those of the empty sample. With the assumption of additivity rule, the contribution of absorbed benzene was estimated by subtracting the heat capacity of the empty sample from that of the absorbed sample. The heat capacity of absorbed benzene determined in this way is shown in Fig. 6 together with that of absorbed benzene in Cuchd and that of bulk benzene. The three sets of data are in rather good agreement, which implies that absorbed benzene behaves like bulk benzene. It should be noted that the absorbed benzene shows no melting phenomenon, which might be due to the general rule; one-dimensional system should have no cooperative phase transition. Thus the benzene molecules in the tunnels should be considered as isolated one-dimensional chains. In the case of the absorbed benzene in Cuchd, 100% benzene was absorbed and thus about 5% of benzene overflown from the tunnels during the cooling process for the heat capacity measurements. The small melting anomaly is

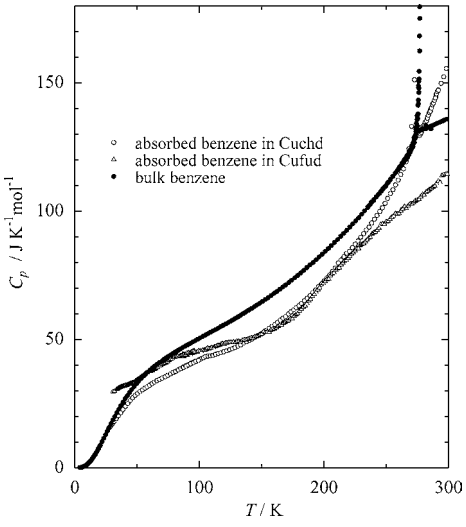

Fig. 6. Heat capacity of absorbed benzene in Cufud (triangle), in Cuchd (circle), and of bulk benzene (closed circle).

due to overflown benzene, which behaved as bulk sample of benzene.

In conclusion, the samples of Cufud and Cuted were synthesized and the heat capacity and the magnetic susceptibility were measured. The results show that no phase transition occurs in the both sample, while a structural phase transition has been reported for Cuchd, which is a member of this family of compounds. Comparison between lattice heat capacities reveals that the lattice of Cuted is less stiff than that of either Cufud or Cuchd. The reversibility of absorption/desorption of large amount of molecules is confirmed for benzene, toluene, and carbon tetrachloride, etc. We also point out that the absorbed molecules can be considered as one-dimensional molecular chains, and that no phase transition or melting phenomenon has been observed.

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