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Low-temperature heat capacity of heptacopper(II) complex $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\textsc{d}\text{-pen-disulfide})_3]$

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Abstract A single crystal calorimetry of a heptacopper(II) complex of $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\textsc{d}\text{-pen-disulfide})_3]$ which has a double-cubane structure supported by D-penicillaminedisulfides has been performed at low-temperature region below 8 K. This compound is a metal complex which contains seven Cu(II)s in a cluster unit. These Cu(II)s are magnetically coupled each other by strong intra-complex interactions. The heat capacities under magnetic fields exhibit Schottky type anomalies explained by the Zeeman splitting of the doublet ground state of the complex. The *g*-value of the ground state is evaluated as 1.86 from the systematic analysis of the Schottky peak under magnetic fields. The first excited state of the cluster seems to be separated at least by several Kelvins, which is consistent with the theoretical calculations and magnetic susceptibility results.

Keywords Heat capacity · Metal complex · Schottky anomaly

Introduction

Polynuclear metal complexes which contain multiple transition metals in a cluster are synthesized and characterized extensively in these years. Among various kinds of polynuclear complexes, those consisting of magnetic atoms, such as Fe, Mn, Ni, and V etc., give promising candidates for studying molecular magnetism. One of the unique magnetic behaviors realized in the polynuclear metal complexes is the single-molecule magnet (SMM) feature [1–3], which has been extensively studied in this decade, for example, in Mn_{12} and Fe_8 clusters. In them, strong intra-complex interactions of spins produce high-spin state with large quantum number, and the anisotropy of spins lead the characteristic behavior dominated by the slow dynamics of 10^{-3}–10^{2} s region. The research on the electronic state of metal cluster complexes containing open shell ions is attracting extensive interests also in application fields. The existence of oxidized and reduced states as a cluster can bring about a possibility of charging materials [4]. Furthermore, the understanding of the electronic states of polynuclear cluster complexes is also important to solve the mechanism of living system from the standpoint of bio-inorganic chemistry. The spin states in these strongly correlated molecular systems are studied, for example, in iron–sulfur cluster such as [8Fe–7S] [5].

Development of new polynuclear metal complexes has been extensively performed, and novel structures and functions have been observed. Among them, those containing multiple Cu(II) cations interests us because the quantum nature of $S = 1/2$ spins coupled with the structural peculiarity of the complex can give an interesting spin state due to the strong electron correlations in the cluster. It is especially interesting when the frustrated character of spins appears owing to a structural restriction. Recently, Igashira-Kamiyama et al. have reported a new type of hepta-Cu(II) cluster structure based on the double-cubane framework [6]. The chemical formula of the compound is $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\textsc{d}\text{-pen-disulfide})_3]$ (we denote this compound as $\{Cu_7\}$ hereafter). In this structure, the central Cu(II) shares the corners of two cubane units expanding to the opposite directions and other six Cu(II)s are located on the corner of these cubanes to form double prismatic structure is displayed schematically as in Fig. 1. Three

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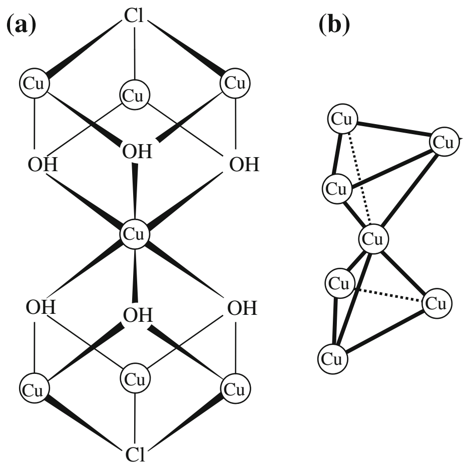

Fig. 1 **a** A schematic drawing of the double-cubane structure of $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\text{D-pen-disulfide})_3]$. **b** A drawing of the triangular cylinder structure consisting of seven Cu(II) ions

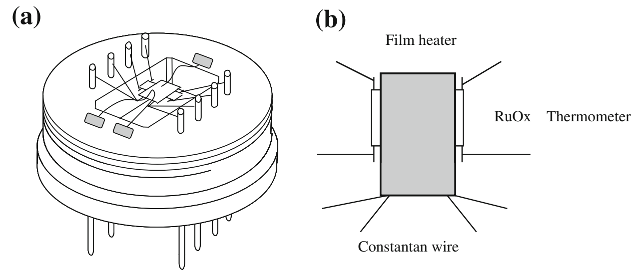

Fig. 2 The schematic illustration of the (**a**) thermal relaxation calorimetry cell and (**b**) the sample stage

Cu(II)s form a distorted triangular structure with similar magnitude of magnetic interactions in both sides of the central Cu(II). The double-cubane framework is supported by D-penicillaminedisulfides. Therefore, two triangular structures consisting of six Cu(II) ions in all are magnetically linked through the central Cu(II) ion of the triangular prism. Although many complexes with triangular spin units are synthesized and studied up to now, the triangular prism structure is quite rare due to the difficulty in chemical syntheses of such asymmetric structure. Furthermore, this structure does not have intra-cluster inversion center, which is very unique among various cluster which has triangular type structures.

The low-temperature heat capacity measurement is an important method to study the ground state and energy schemes of these multi-spin clusters [7]. In order to determine the ground state of this new type of double-cubane structure, the information of magnetic entropy at low temperatures is important. We have tried to perform calorimetry using the thermal relaxation technique to determine the ground state of the complex.

Experimental

In this study, we have used several pieces of single crystals of $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\text{D-pen-disulfide})_3]$ with total weight of 130 µg. The synthesis and characterization results including crystallographic data and magnetic properties were reported in [6]. According to the results of a theoretical calculation based on the magnetic susceptibility measurements, the ground state of the complex is doublet with $S = 1/2$ and the first excited state is $S = 3/2$. The very weak antiferromagnetic interaction exists between complexes which are observed by the gradual decrease of χT value with decreasing temperatures [6]. For heat capacity measurements, we have used thermal relaxation calorimeters constructed by ourselves. In order to get the absolute value of heat capacity using tiny single crystals, the size of the sample stage was reduced to about 600 µm × 1.2 mm as shown in Fig. 2. The details of the calorimeters have been published in literatures [8–10]. The heat leak from the sample stage to the heat sink is given by thin constantan wires with a diameter of 13 µm. In order to adjust the heat leak, we can use the constantan wires with different diameters of 25 and 50 µm. The calorimetry cell consisting of a chip type resistance of ruthenium oxide and Ni–Cr film heater is mounted on the ^{3}He refrigerator available in the variable temperature insert (VTI) system and a dilution refrigerator. The magnetic fields were applied perpendicular to the largest surface of the plate-type crystal using the superconductive magnet. In each experiment, we have conducted a blank measurement of the sample stage with proper amount of Apiezon N grease before setting the crystals to obtain accurate background data. The temperature dependence of the blank heat capacity is fitted by the 8–12th polynomials depending on temperature region and subtracted from the total heat capacity to determine the absolute value of C_p of the sample.

Results and discussion

In Fig. 3, we show temperature dependence of the heat capacity in a C_pT^{-1} versus T^2 plot. The heat capacity does not show any thermal anomaly in the whole temperature region studied. One can notice that the low-temperature part of C_pT^{-1} shows an upturn at low temperatures. The existence of the upturn at the lowest temperature region demonstrates that the degeneracy of spin states surely exists in this material. The absence of the sharp peak structure down to this low-temperature region suggests that there is no long range ordering between the spins localized on each double-cubane unit, in spite of a weak antiferromagnetic interaction

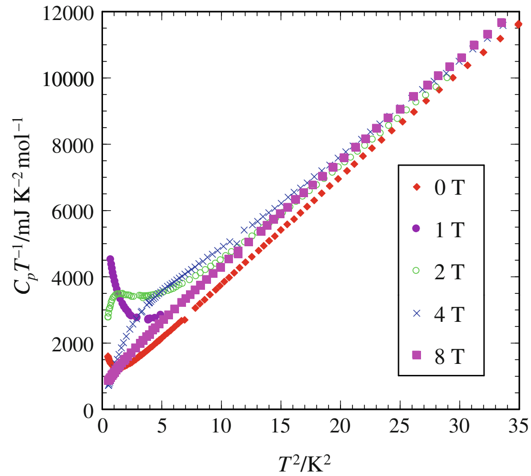

Fig. 3 Temperature dependence of heat capacity of $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\text{D-pen-disulfide})_3]$ obtained under various magnetic fields

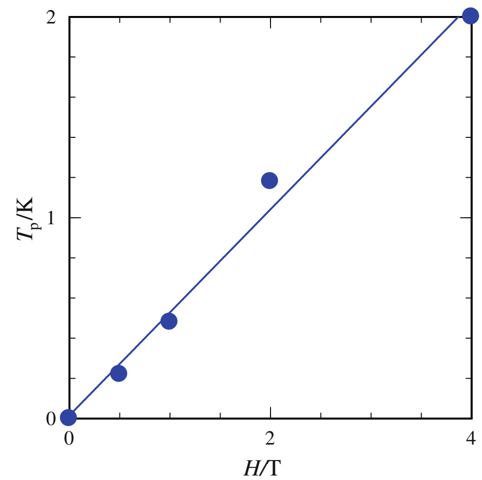

Fig. 5 Variation of the heat capacity peak temperature plotted as a function of external magnetic fields

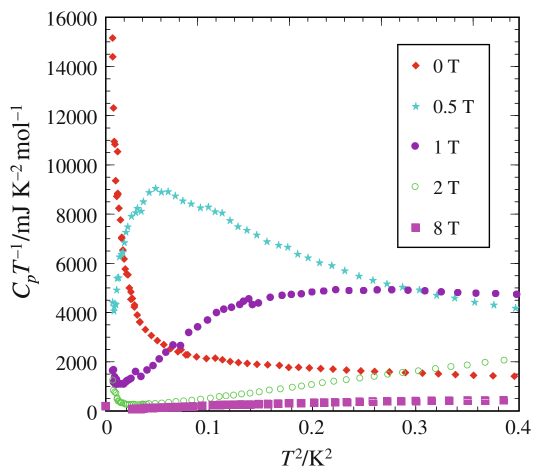

Fig. 4 Low-temperature data of $[Cu_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6\text{-}(\text{D-pen-disulfide})_3]$ obtained by a dilution refrigerator

is suggested from the magnetic susceptibility data. The C_pT^{-1} versus T^2 plot do not show simple linear behavior expressed by the low-temperature approximation of the Debye model owing to the rather complicated low-energy phonons characteristic of the molecular based compounds. In the figure, we also show data obtained under magnetic fields up to about 8 T. The upturn of C_pT^{-1} at zero magnetic fields grows larger at 1 T and changes to a broad peak structure above 2 T which seems to be a Schottky structure characteristic of the thermal excitations from the ground state to the excited state over a distinct energy gap. To see the low-temperature properties in more details, we have performed heat capacity measurements using a dilution refrigerator. The experimental results between 90 mK and 0.6 K is shown in Fig. 4. From this figure, we can notice of a systematic change of heat capacity under magnetic fields. The upturn of C_pT^{-1} grows with the decrease of temperatures even at weak magnetic fields below 1 T, which demonstrate the ground state of the spin level is degenerated. The fitting of the lowest temperature part of 0 T curvature below 0.4 K gives the energy splitting of about 60 mK, which probably corresponding to the splitting due to hyperfine coupling with the nuclear levels. The Schottky peak temperature is 0.22 K at 0.5 T and 0.51 K at 1 T, respectively. The peak temperatures increase almost linearly against the external magnetic fields, which demonstrate that the inter-cluster interactions are weak to produce magnetic correlations between clusters. The fitting of the peak temperature gives a slope of 0.486 KT^{-1} as shown in Fig. 5. The magnetic entropy related to the Schottky peak at 0.5 T is evaluated as 4.25 J K^{-1} mol^{-1} at 0.65 K. This value is 70% of $R\ln2$, which may well be considered that the ground state of the complex is doublet. Since the temperature region obtained by our system using the tiny sample is limited, accurate estimation of lattice heat capacity is difficult only from the present data. However, the magnetic field dependence and proper amount of entropy demonstrates that the ground state is a doublet with $S = 1/2$ ground state. From the linear slope shown in Fig. 5, we have evaluated that the g-value of the ground state is 1.86, which is consistent with the $S = 1/2$ ground state.

The theoretical approach to describe the spin states of this polynuclear complex is performed to explain the physical properties of these complexes. The strong electron correlations effects are included by the broken symmetry method by Shoji and Yamaguchi based on the Heisenberg exchange Hamiltonian of the Cu(II)–Cu(II) magnetic interactions in the complex. According to their results, adoption of all type of intra-cluster magnetic interaction between neighboring Cu(II) in the cluster is necessary to describe the temperature dependence of magnetic susceptibility. Their results also show that the ground state should be $S = 1/2$ and the first excited state of $S = 3/2$ is well-separated, which is quite consistent with the present heat capacity result.

The spin state of these kinds of complexes with complicated cluster structure, especially those possessing the triangular structure is attracting wide interests in the fields of magnetism. The magnetic state based on the exchange coupled triangular spins of VO^{2+} is frustrated in the cluster. The similar $\{V_6\}$ cluster constructed by the two triangles in a molecule has also been studied [11, 12]. The behavior of the degenerated $S = 1/2$ doublets and their low-energy scheme including the interesting quantum tunneling effects were studied under relatively strong magnetic fields. In the present hepta-Cu(II) cluster, $\{Cu_7\}$ makes a $S = 1/2$ state, although the inter-relation of the two triangles is different from the $\{V_6\}$ system. The magnetic behavior under high magnetic fields larger than 8 T seems to be important to see the energy crossing behavior in this complex.

Summary

We have performed a single crystal calorimetry of $\{Cu_7\}$ complex which has triangle cylinder structure. From the low-temperature heat capacity under magnetic fields up to 8 T, we have observed a systematic increase of Schottky heat capacity peak with the increase of magnetic fields. The quantitative analysis of the heat capacity peak, the ground state was concluded to be a doublet expressed by $S = 1/2$, which is consistent with the magnetic susceptibility data and quantum chemistry calculation.

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