Calorimetric Study of a Halogen-Bridged MMX Chain Complex Having Alkyl Chains, Pt₂(*n*-PrCS₂)₄I (*n*-Pr = Propyl Group)†

Satoaki Ikeuchi,‡ Kazuya Saito,*,‡ Yasuhiro Nakazawa,§ Minoru Mitsumi,‖ Koshiro Toriumi,‖ and Michio Sorai‡

Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, Department of Chemistry, Graduate School of Science and Technology, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152-8850, Japan, Department of Material Science, Himeji Institute of Technology, Harima Science Park City, Hyogo 678-1297, Japan

The heat capacity of a halogen-bridged quasi-one-dimensional (Q1D) mixed-valence binuclear metal complex (the so-called MMX chain), Pt₂(*n*-PrCS₂)₄I, was measured by adiabatic calorimetry. A higher order phase transition due to structural disorder was observed at 209 K. Another first-order phase transition having a large tail on the low-temperature side was detected at 358.8 K. Their enthalpy and entropy of transition were determined and analyzed. As evidenced by the magnitude of the entropy of transition, similar structural disorder occurs at the corresponding phase transition in Pt₂(*n*-PrCS₂)₄I and Pt₂(*n*-BuCS₂)₄I, but the shape of thermal anomaly is largely different between the two. The magnitude of the entropy of transition shows that the change of both structural disorder and electronic states occurs simultaneously in a gradual manner on the low-temperature tail of the thermal anomaly at 358.8 K. The change in entropy assignable to the Q1D electron system was estimated as about 2.3 J K⁻¹ mol⁻¹.

1. Introduction

In quasi-one-dimensional (Q1D) electron systems have been found various interesting electronic, magnetic and optical properties.[1] For example, strong electron−lattice interaction, electron correlation, and spin−lattice interaction cause Peierls transition related to charge density wave (CDW), spin density wave (SDW), and spin-Peierls transition, respectively. Systems so far studied cover metal chalcogenides, organic conductors, inorganic and organic polymers, and transition metal complexes.

Halogen-bridged 1D mixed-valence binuclear metal complexes, the so-called MMX chains, have recently attracted much interest. There exist metal−metal bonds in the MMX chains. This gives possibilities of much varieties of their electronic states such as metal, Mott−Hubbard insulator, bond-order-wave (BOW), X−CDW (CDW on X), M−CDW, X−SDW, M−SDW, spin bond order wave (SBOW), etc.[2,3] These electronic states have been predicted to be realized through the competition between electron−lattice interaction, electronic correlation, and spin−lattice interaction. The half-filled Q1D conduction band is of an antibonding combination of transition metals Md_{z^2} orbitals within a unit cell. Representatives of the MMX chain compounds having been studied are A₄[Pt₂(pop)₄X]·nH₂O (A = Li, K, Cs, NH₄; pop = H₂P₂O₅²⁻, diphosphonato; X = Cl, Br, I),[4−8] and M₂(RCS₂)₄I (M = Pt, Ni; R= alkyl chain).[9−22]

M₂(RCS₂)₄I has four alkyl chains (R) in ligands. Elongation of alkyl chains in ligands is considered to enhance the one-dimensionality of the electronic system on the MMX chains because of weak van der Waals S−S contacts between neighboring chains. Mitsumi and Toriumi[17−22] thus started a systematic study on a homologous series of M₂(RCS₂)₄I having long chains. Besides, the elongation of the alkyl chains introduces increasing motional degrees of freedom in the system. Interplay between electronic degrees of freedom and molecular dynamics is also of current interest.[23−25] The present paper is concerned with such a Pt compound, Pt₂(*n*-PrCS₂)₄I, with the *n*-propyl chain (CH₃CH₂CH₂−).

Recently, the heat capacity of Pt₂(*n*-BuCS₂)₄I (*n*-Bu = *n*-butyl group) measured by adiabatic calorimetry was reported by the present authors.[22] The first-order phase transitions involving disordering of the dithiocarboxylato group (CS₂) and the butyl chain occur at 213.5 and 323.5 K. The model of the structural disorder of each phase was established on the basis of the magnitude of the entropy of transition. From the analysis of entropy of transition due to structural disorder, the entropy contribution intrinsic to change between magnetic state and nonmagnetic state of the MT−RT phase transition at 213.5 K, where both changes in structural disorder and electronic state occur simultaneously, was estimated.

For the title compound Pt₂(*n*-PrCS₂)₄I, three phases have been known through the transport and structural studies.[18,19] The structures of the room-temperature (RT) phase and the high-temperature (HT) phase have been determined by the single-crystal X-ray analyses.[18] Their structures have been determined as shown in Figure 1. The HT phase (Figure 1b) appearing above ca. 359 K has uniform structure along the 1D chain (the *c*-axis of tetragonal system).[18] There is, in principle, an unpaired electron with spin ¹/₂ per unit complex including two Pt atoms. The electrical conductivity is rather good in this phase though its temperature dependence is not "metallic." The dithiocarboxylato groups show a structural disorder concerning their twist with respect to the Q1D MMX chain, as in a manner similar to that of Pt₂(*n*-BuCS₂)₄I.[20] On cooling from the HT phase, the

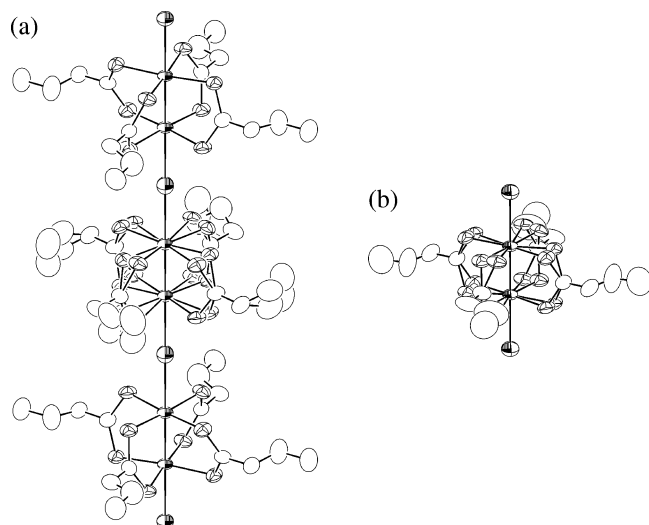* Corresponding author. E-mail: kazuya@chem.sci.osaka-u.ac.jp.
‡ Osaka University.
§ Tokyo Institute of Technology.
‖ Himeji Institute of Technology.

(a)

(b)

Figure 1. Molecular structures of $Pt_2(n\text{-}PrCS_2)_4I$ determined at (a) 293 K (RT phase) and (b) 377 K (HT phase).[18] Complexes only within a unit period along the MMX chain (*c*-axis) are shown. The structural solution and refinement on the RT phase were done while a small number of superlattice reflections corresponding to the doubled period along the *c*-axis were neglected.

resistivity and thermoelectric power exhibit a jump around 359 K due to a phase transition. At room temperature, the electric conductivity of $Pt_2(n\text{-}PrCS_2)_4I$ is ca. 0.23 S cm^{-1}. The crystal structure of this phase was determined at 293 K, as shown in Figure 1a.[18] The lattice constant along the *c*-axis is tripled in the MMX unit. This periodicity describes only the structural disorder concerning the dithiocarboxylato groups and the propyl chains belonging to only the center complex in a unit cell length, similarly to $Pt_2(n\text{-}BuCS_2)_4I$.[20] Four dithiocarboxylato groups belonging to the two ordered complexes are twisted right or left. That is, the linear chain structure is represented by the twisted manner of $Pt_2(n\text{-}PrCS_2)_4I$ units as a sequence of −disorder−right−left− as in $Pt_2(n\text{-}BuCS_2)_4I$.[20] The complex is reported as being diamagnetic below room temperature.[18,19] Here, it is noteworthy that the diamagnetism implies an evenly multiplied periodicity along the MMX chain because spins on the adjacent MMX units are to be strongly coupled in the diamagnetic state. In fact, weak superlattice reflections corresponding to the doubled periodicity are observed even at room temperature,[18] though they have not been used for structure analysis to obtain the average structure shown in Figure 1a. The correct unit cell therefore has an integer multiple of two MMX units. This is consistent with the unusually large temperature factors along the MMX chains of I atoms with respect to those of Pt atoms in the structure determined assuming the periodicity of 3.[18] On further cooling, some physical properties show anomalies around 200 K, implying the presence of a phase transition similar to those in $Pt_2(n\text{-}BuCS_2)_4I$.[20]

In this work, the heat capacity of $Pt_2(n\text{-}PrCS_2)_4I$ was measured with adiabatic calorimetry to characterize the phase transitions detected in the transport and the magnetic studies. The results are described in detail, and the validity of the analysis of $Pt_2\text{-}(n\text{-}BuCS_2)_4I$ on structural disorder[22] is assessed. The comparison is made of the entropy involved and the shape of thermal anomaly in $Pt_2(n\text{-}PrCS_2)_4I$ and $Pt_2(n\text{-}BuCS_2)_4I$ to discuss the electron−lattice "coupling."

2. Experimental Section

The sample synthesized as described previously[18] was loaded into a gold-plated copper calorimeter vessel, which was evacu-
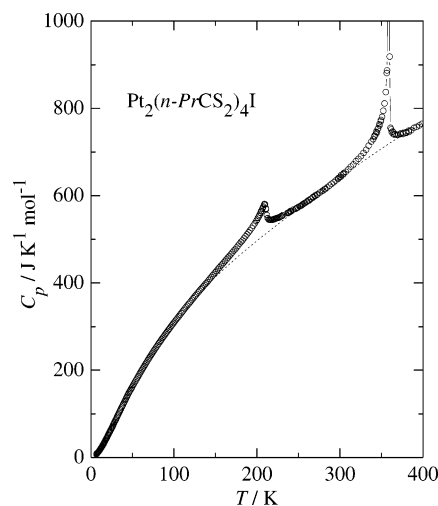
Figure 2. Measured molar heat capacities of $Pt_2(n\text{-}PrCS_2)_4I$ (open circle) and the assumed normal heat capacity (dotted curve) to separate the excess heat capacity due to the LT-RT and RT-HT phase transitions.

ated for about 1 h and sealed after adding a small amount of helium gas (10^5 Pa at room temperature) for assisting thermal equilibration within the vessel. The mass of the sample loaded was 2.0055 g (2.0177 mmol) after buoyancy correction.

The working thermometer mounted on the calorimeter vessel was a platinum resistance thermometer (Minco, S1059). Its temperature scale is based upon the ITS-90. The details of the adiabatic calorimeter used and its operations are described elsewhere.[26]

The measurement was carried out by the so-called intermittent heating adiabatic method. The temperature increment by a single energy input (Joule heating) was less than 1% of temperature. Thermal equilibrium inside the vessel was attained within a normal time (1−10 min depending on temperature) after energy input was turned off except for the close vicinity of the RT-HT transition temperature. The sample contributed 14% of the total heat capacity including that of the vessel at 50 K, 12% at 100 K, 14% at 200 K, 16% at 300 K, and 16% at 400 K.

3. Results

The heat capacity of $Pt_2(n\text{-}PrCS_2)_4I$ was measured between 6 and 400 K. Typical results are shown for the whole temperature range studied in Figure 2. Two anomalies can be recognized in temperature dependence of the heat capacity.

The anomaly around 209 K has a large tail on both the low-temperature sides down to about 90 K and the high-temperature side up to about 280 K as seen in Figure 2. Because no latent heat was detected, this anomaly is attributed to a higher-order phase transition. The phase below this phase transition is designated as the low-temperature (LT) phase hereafter.

Around 359 K, a sharp thermal anomaly is observed, as shown in Figure 2. This anomaly is obviously attributed to the phase transition from the RT phase to the HT phase, taking the previous study into account.[18] In this transition region, the measurements were repeated three times to determine the transition temperature. The temperature of the transition was determined as 358.8 ± 0.2 K. The time for thermal equilibration around the temperature of transition was longer than that of the normal region. The order of this transition is, therefore, regarded as a first-order though no supercooling was observed despite some trials.

To see the magnitude and the shape of the anomalies around 209 and 358.8 K, a normal heat capacity was assumed as a

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TABLE 1: Temperatures, Enthalpies, and Entropies of Transitions around 200 K and above Room Temperature in Pt$_2$(n-PrCS$_2$)$_4$I and Pt$_2$(n-BuCS$_2$)$_4$I[22,a]

	LT (MT) phase → RT phase			RT phase → HT phase		
	$T_{trs}/$ K	$\Delta_{trs}H/$ kJ mol^{-1}	$\Delta_{trs}S/$ J K^{-1} mol^{-1}	$T_{trs}/$ K	$\Delta_{trs}H/$ kJ mol^{-1}	$\Delta_{trs}S/$ J K^{-1} mol^{-1}
Pt$_2$(n-PrCS$_2$)$_4$I	209	2.75	14.6	358.8	3.50	10.0
Pt$_2$(n-BuCS$_2$)$_4$I	213.5	4.29	20.09	323.5	2.41	7.46
model			15.36			7.68

[a] Also shown for comparison is the expected entropy of transitions according to the model of structural disorder. For the details of the model, see the text.
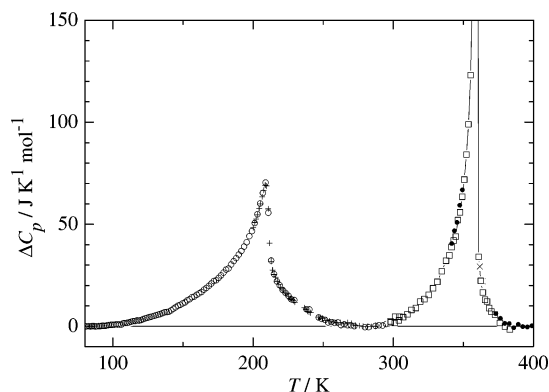
Figure 3. Excess heat capacities around the LT-RT and RT-HT phase transitions of Pt$_2$(n-PrCS$_2$)$_4$I. Different symbols imply different runs of measurements.
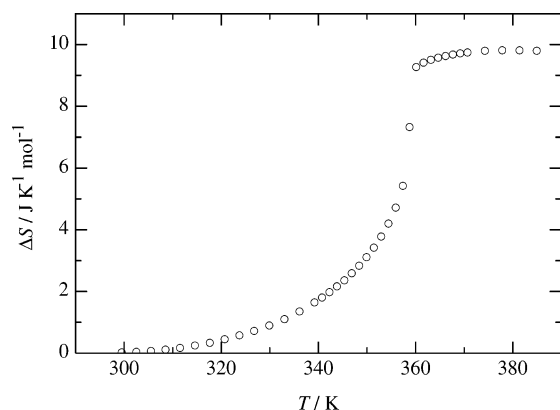
Figure 4. Temperature dependence of the entropy gain due to the RT-HT phase transition of Pt$_2$(n-PrCS$_2$)$_4$I obtained in a single run of measurements.

smooth interpolating curve between 80 and 400 K. In practice, the baseline was approximated by a fourth-order polynomial of temperature, as shown by a dotted curve in Figure 2. The excess heat capacities were separated by subtracting the normal portion from the experimental data and are shown in Figure 3. The data obtained in different series of measurement are plotted by different symbols there.

The integration of the excess heat capacity with respect to temperature and logarithmic temperature yields the excess enthalpy and entropy as 2.75 kJ mol^{-1} and 14.6 J K^{-1} mol^{-1}, respectively, for the LT-RT phase transition.

For the RT-HT phase transition, similar integrations yield the enthalpy and entropy of transition as 3.50 kJ mol^{-1} and 10.0 J K^{-1} mol^{-1}, respectively. An example of the results is shown in Figure 4. The vertical increase at 358.8 K corresponds to the contribution of the latent heat. The excess enthalpy and entropy involved in the tail of thermal anomaly was similarly estimated by integrating the tail as 1.92 kJ mol^{-1} and 5.6 J K^{-1} mol^{-1}, respectively. As the result, the changes in enthalpy and

entropy corresponding to the latent heat were estimated as 1.58 kJ mol^{-1} and 4.4 J K^{-1} mol^{-1}, respectively. This partition provides important information on the changes occurring on the course of this phase transition, as will be discussed later.

The following notice should be given here. As described above, the enthalpy and entropy of transition in Pt$_2$(n-PrCS$_2$)$_4$I are obtained by integration of the excess heat capacities over wide temperature ranges due to the presence of large tails. Some uncertainty is unavoidable to draw a baseline to separate excess heat capacities. The above estimates are considered to put minimum bounds for the corresponding quantities.

4. Discussion

A. Structural and Electronic Contributions to Entropies of Transitions. The molecular structures in the RT and the HT phases of Pt$_2$(n-PrCS$_2$)$_4$I have been determined by single-crystal X-ray experiments (Figure 1),[18] whereas it is not for the LT phase. For the RT and the HT phases, the reported patterns of structural disorder are the same as those of Pt$_2$(n-BuCS$_2$)$_4$I.[20] Although no experimental report is available, the LT phase is reasonably assumed to be ordered because neither any phase transition nor glass transition was detected, implying that the LT phase obeys the third law of thermodynamics.

The expected entropy due to structural disorder was calculated by the determined model of Pt$_2$(n-BuCS$_2$)$_4$I,[22] because the pattern of structural disorder of each phase in Pt$_2$(n-BuCS$_2$)$_4$I[20] and Pt$_2$(n-PrCS$_2$)$_4$I is the same.[18] This model was discussed in detail in ref 22. The experimental and model entropies of the LT-RT and RT-HT phase transitions are compared in Table 1. For Pt$_2$(n-PrCS$_2$)$_4$I, the entropy of transition for the LT-RT phase transition shows a good agreement (though slightly smaller) with that from the model, whereas the entropies of transition for the RT-HT phase transition are larger than that expected from the model. The trend is reversed in Pt$_2$(n-BuCS$_2$)$_4$I.[22] Here, the following facts should be reminded: The LT-RT phase transition of Pt$_2$(n-PrCS$_2$)$_4$I and the RT-HT phase transition of Pt$_2$(n-BuCS$_2$)$_4$I involve only the change in structural disorder whereas the RT-HT phase transition of Pt$_2$(n-PrCS$_2$)$_4$I and the MT-RT phase transition of Pt$_2$(n-BuCS$_2$)$_4$I accompany changes in both structural and electronic/magnetic degrees of freedom. Namely, the entropies of phase transitions involving only the structural change are favorably accounted for by the present model. Besides, the phase transitions accompanying the other change(s) exhibit larger entropies of transition than those expected from the model. These clearly show that the present model is adequate as far as the structural disorder in Pt$_2$(n-PrCS$_2$)$_4$I and Pt$_2$(n-BuCS$_2$)$_4$I is concerned. The difference beyond the present model is therefore considered as contributions closely connected to the Q1D electron systems. Detailed discussion on properties of each phase transition of Pt$_2$(n-PrCS$_2$)$_4$I will be given later.

The success of the present model indicates that the entropy (disorder) once gained in alkyl chains in the RT phase is transferred to the dithiocarboxylato group upon the RT-HT phase
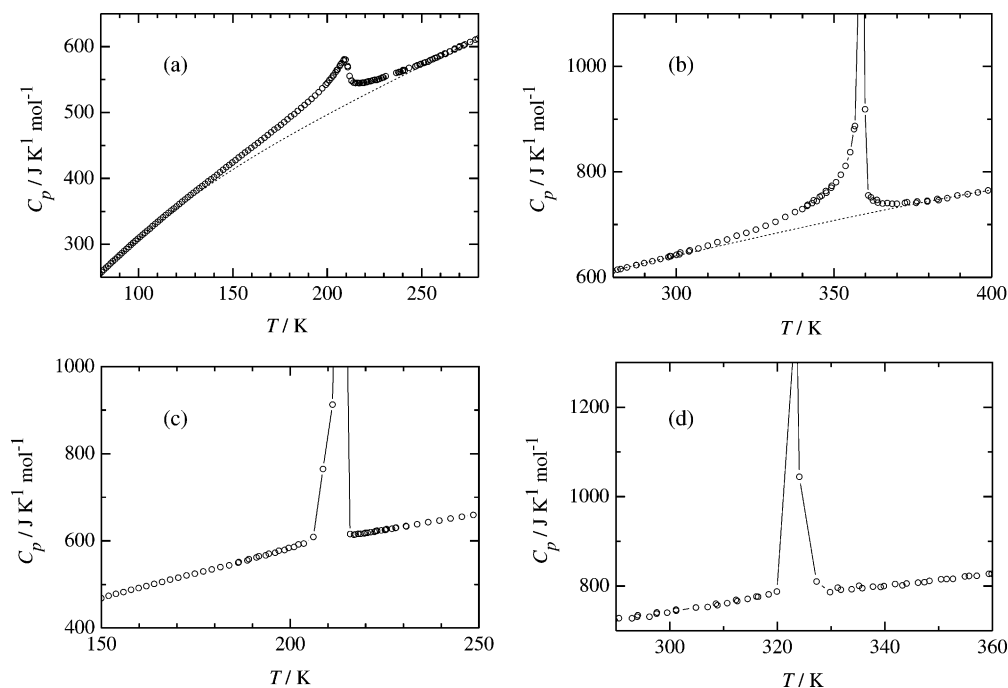
Figure 5. Comparison of the shape of heat capacity anomalies around (a) the LT-RT phase transition and (b) the RT-HT phase transition of $Pt_2(n\text{-}PrCS_2)_4I$ and (c) the MT-RT phase transition and (d) the RT-HT phase transition of $Pt_2(n\text{-}BuCS_2)_4I$.[22] The assumed normal heat capacities to separate excess heat capacities are also shown in (a) and (b).

transition. A similar entropy transfer has already been identified as an important mechanism for determining the phase sequence of thermotropic liquid crystals containing isotropic meso-phases.[27,28]

B. LT-RT Phase Transition. The entropy of the LT-RT phase transition of $Pt_2(n\text{-}PrCS_2)_4I$ is successfully explained by the disorder model described in the previous section as well as $Pt_2(n\text{-}BuCS_2)_4I$. The behavior of their phase transitions is, however, largely different. Their measured heat capacities around the phase transition are compared in Figure 5a,c. Though the LT-RT phase transition in $Pt_2(n\text{-}PrCS_2)_4I$ is of higher order, the MT-RT phase transition in $Pt_2(n\text{-}BuCS_2)_4I$ is first-order. It is emphasized that, despite such a large difference, the discussion on entropy stands well.

It is usually hard to construct a model that involves multiple order parameters and exhibits a continuous (typically second-order) phase transition. In this context, one may say that the different order of phase transitions originates in the fact that the LT-RT phase transition in $Pt_2(n\text{-}PrCS_2)_4I$ only involves the structural disordering whereas the MT-RT phase transition in $Pt_2(n\text{-}BuCS_2)_4I$ has additional change in electronic states. Such a discussion, however, seems inadequate here. Even though such a mechanism works to bring a first-order phase transition, gradual change(s) in order parameter(s) may occur, as exempli-fied by the RT-HT phase transition in $Pt_2(n\text{-}PrCS_2)_4I$ shown in Figure 5b.

In a previous paper,[22] the present authors pointed out on the basis of the reported crystal structures that the MT-RT phase transition is first-order (first-kind) according to Landau's phenomenology.[29] If the symmetry relation between LT and RT phases is the same in $Pt_2(n\text{-}PrCS_2)_4I$, the same conclusion is deduced for the order of the LT-RT phase transition.

The crystal of the RT phase has the periodicity of 6 or its integer multiple for $Pt_2(n\text{-}PrCS_2)_4I$. This period is a common multiple for the tripled periods of structural disorder in the MMX unit and the doubled period as deduced from the presence of a small number of Bragg reflections. The importance of this doubled periodicity is proven by the fact that the compound is
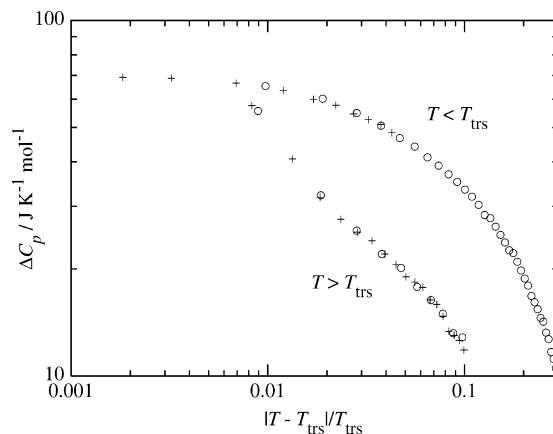
Figure 6. Critical plot of excess heat capacities of $Pt_2(n\text{-}PrCS_2)_4I$ around the LT-RT phase transition. Different symbols distinguish different runs of measurement.

essentially diamagnetic even at room temperature.[18,19] It is noted here that the preference for even periodicity should be attributed to the Q1D electron system on the MMX chain. The higher order nature of the LT-RT phase transition demonstrated in the present result requires the compatible symmetry relation with a phase transition of the second kind according to Landau's phenomenology.[29] Because the RT phase has a periodicity of 6 or its integer multiple, the periodicity of the LT phase is also of an integer multiple of 6.

Now, a brief discussion on the shape of the thermal anomaly is given. A jump in heat capacity amounting to ca. 40 J K^{-1} mol^{-1} can be recognized at the transition temperature in Figure 5a, though the presence of appreciable tail is also evident even above the transition temperature. The LT-RT phase transition of $Pt_2(n\text{-}PrCS_2)_4I$ may be regarded as a second-order transition. The diverging trend of excess (critical) heat capacity is weak as seen in Figure 6. The tailing above the transition temperature and diverging temperature dependence below it of the heat capacity anomaly suggest that the fluctuation be important probably because the system has some character of a low-

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dimensional system. The structural anisotropy (chain structure) will be related to this low-dimensional character of the LT-RT phase transition.

C. RT-HT Phase Transition and Electron−Lattice "Coupling". In the context of the symmetry relation discussed in the previous section, there is no restriction on the order of the RT-HT phase transition in both $Pt_2(n\text{-PrCS}_2)_4I$ and $Pt_2(n\text{-BuCS}_2)_4I$. Namely, the RT-HT phase transitions can be of the second kind. They are, in reality, first-order with a different appearance of thermal anomalies as compared in Figure 5b,d. $Pt_2(n\text{-PrCS}_2)_4I$ exhibits an appreciable tail in the low-temperature side.

The experimental entropy of the RT-HT phase transition is larger than that expected from the model of disorder, as already described. The excess (2.3 J K^{-1} mol^{-1}) should be attributed to the degree of freedom closely connected to the Q1D electron system on the MMX chain. The presence of this entropy excess is evidence that the nature of the Q1D electron system on the MMX chain surely changes upon the RT-HT transition, though even its mechanism has not been clarified because of the lack of microscopic experimental results.

The contribution from the nonstructural origin to the entropy of transition differs by a factor 2 from the similar excess in the case of the MT-RT phase transition of $Pt_2(n\text{-BuCS}_2)_4I$.[22] In a previous paper,[22] the present authors discussed that the entropy change assignable to the Q1D electron system in $Pt_2(n\text{-BuCS}_2)_4I$ could not be explained successfully by any existing theories (models). It is interesting that the magnetic susceptibility of $Pt_2(n\text{-PrCS}_2)_4I$ is smaller than that of $Pt_2(n\text{-BuCS}_2)_4I$ roughly in proportion to the entropy change assignable to the Q1D electron system.

The experimental entropy gain can be partitioned into two parts, that of the low-temperature tail of the thermal anomaly (5.6 J K^{-1} mol^{-1}) and that of the latent heat (4.4 J K^{-1} mol^{-1}). It is therefore interesting to see in which temperature (region) the structural disorder proceeds. The entropy of transition by the disorder model (7.68 J K^{-1} mol^{-1}) is larger than both contributions of the experimental one. This means that the structural ordering proceeds in both temperatures (region). At least in one region, therefore, the structural change and change in the Q1D electron system occur simultaneously.

In the temperature region of the low-temperature tail of the thermal anomaly, the gradual decrease in the intensity of the superlattice reflections corresponding to the tripled periodicity was reported upon heating.[20] Because the tripled periodicity is caused by the arrangement of ordered and disordered complexes along the MMX chain, as seen in Figure 1a, this observation can be regarded as experimental evidence of gradual disordering in this region. On the other hand, a slight increase in magnetic susceptibility was also reported upon heating from room temperature.[21] This implies that the change in the Q1D electron system on the MMX chain also proceeds gradually in this temperature region.

The present model of disorder under discussion assumes the transfer of structural entropy from alkyl chains to dithiocarboxylato groups upon the RT-HT transition. This mechanism is easy to imagine for a purely first-order transition such as that observed in $Pt_2(n\text{-BuCS}_2)_4I$[22] but not for a continuous transition. This is also not for the RT-HT phase transition of $Pt_2(n\text{-PrCS}_2)_4I$ having a considerable tail below the transition temperature, though the phase transition completes as a first-order transition. This apparent conflict may be solved in two ways. First, the structural disordering (upon heating) and instability intrinsic to the Q1D electron system on the MMX chain grows indepen-

dently below the transition temperature. The balance is adjusted at the transition temperature as the latent heat. In the other way, the two instabilities are strongly coupled with each other, resulting in the observed tailing. Although no plausible model predicting the latter fascinating scenario is available, it seems possible when the fact is considered that the RT-HT phase transition in $Pt_2(n\text{-BuCS}_2)_4I$, which only involves the structural disordering, is a purely first-order transition without heat capacity tailing, as seen in Figure 5d.

The MT-RT phase transition of $Pt_2(n\text{-BuCS}_2)_4I$ at 213.5 K shares some properties such as simultaneous change in the structure and magnetism with the RT-HT phase transition in $Pt_2(n\text{-PrCS}_2)_4I$.[20−22] On the other hand, the shape of thermal anomaly is different from each other. The thermal anomaly due to the RT-HT phase transition of $Pt_2(n\text{-PrCS}_2)_4I$ (Figure 5b) has a large tail on the low-temperature side, whereas that due to the MT-RT phase transition of $Pt_2(n\text{-BuCS}_2)_4I$ (Figure 5c) has no tail. Because the changes in the Q1D system on the MMX chain may be different, a simple comparison also may be inadequate. The following point is, however, to be considered: According to the model of disorder, alkyl chains (R) in $Pt_2(RCS_2)_4I$ behave as a unit particle undergoing positional disorder. This requires the motional correlation within a chain be very strong (perfect in the ideal case). Elongation of the chain possibly weakens this intrachain correlation, resulting in the increased freedom of the end part of the chain. A shorter chain having less freedom is considered being susceptible to the electronic state of the complex that the chain itself is bonding to. The electron−lattice coupling (in a broad sense) will therefore be more effective in a shorter chain compound than in a longer chain one. It is reported that a homologue with a shorter chain, $Pt_2(EtCS_2)_4I$ (Et = ethyl group), does not undergo a phase transition originating in the structural disorder.[17,20] The different behavior of these compounds can be rationalized along the latter scenario in the last paragraph. Too strong electron−lattice coupling [in $Pt_2(EtCS_2)_4I$] suppresses the disordering, an intermediate one [in $Pt_2(n\text{-PrCS}_2)_4I$] brings about a phase transition with an appreciable effect of the coupling, and a weak one [in $Pt_2(n\text{-BuCS}_2)_4I$] results in a simple (purely structural) disordering transition. Intramolecular motional correlation has been discussed little even in purely structural phase transitions.[30]

5. Conclusion

Heat capacity of a halogen-bridged one-dimensional binuclear metal complex, $Pt_2(n\text{-PrCS}_2)_4I$, was measured by adiabatic calorimetry. Higher-order phase transition and first-order phase transition having a large tail on the low-temperature side, were observed at 209 and 358.8 K, respectively. Although the entropy of transition at 209 K (14.6 J K^{-1} mol^{-1}) is favorably explained by the structural disorder of ligands, that at 358.8 K (10.0 J K^{-1} mol^{-1}) involves an additional electronic/magnetic contribution (2.3 J K^{-1} mol^{-1}) beyond the contribution of the structural disorder. The shape of thermal anomaly shows that, in the LT phase, the period of lattice involves a long periodicity such as 6 in the MMX unit along the one-dimensional chain.

The magnitude of entropies of transitions shows that the model of structural disorder constructed for $Pt_2(n\text{-BuCS}_2)_4I$[22] works quite well for $Pt_2(n\text{-PrCS}_2)_4I$, though the appearance of the disordering process such as the order of phase transition is largely different in two compounds. The model assumes that, upon the phase transition from the room-temperature phase to the high-temperature phase, the entropy reserved in alkyl chain is transferred to dithiocarboxylato groups.

The MMX complex represented as $Pt_2(RCS_2)_4I$ has the structural degrees of freedom concerning the conformation of

the alkyl chains and the orientation of the dithiocarboxylato group. Indeed, in the present complex Pt$_2$(*n*-PrCS$_2$)$_4$I, the change of both structural disorder and electronic states simultaneously occurs in gradual manner on the low-temperature tail of thermal anomaly, though the nature of the change has not been known. To understand the various properties found in MMX systems, further efforts are necessary both experimentally, pursuing the microscopic information concerning the Q1D electron system, and theoretically, while adequately taking into account of both electronic and lattice degrees of freedom. The excess entropy having assigned to the Q1D electron system in the present paper exerts a hard constraint on comprehensive models to be constructed.

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