Alkyl Group as Entropy Reservoir in an MMX Chain Complex, Pt$_2$(*n*-PenCS$_2$)$_4$I[†]

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Heat capacity of halogen-bridged one-dimensional binuclear metal complex (so-called MMX chain) having four *n*-pentyl groups, Pt$_2$(*n*-PenCS$_2$)$_4$I, was measured by adiabatic calorimetry. A first-order phase transition was observed at 207.4 K when measurement was made after cooling from room temperature. The enthalpy and entropy of transition were determined to be 10.19 kJ mol^{-1} and 49.1 J K^{-1} mol^{-1}, respectively. A monotropic phase transition was observed at 324 K on heating, and the entropy of transition was essentially null. The sample once heated above 324 K never returned to the initial phase at room temperature and underwent a higher-order phase transition at 173 K and a first-order phase transition at 220.5 K. The enthalpy and entropy of the first-order phase transition were estimated to be 11.6 kJ mol^{-1} and 52.4 J K^{-1} mol^{-1}, respectively. The magnitude of the entropy gain at the phase transition from the initial room-temperature phase to the high-temperature phase at 324 K shows that in Pt$_2$(*n*-PenCS$_2$)$_4$I a large amount of entropy reserved in alkyl chain is transferred to dithiocarboxylato groups upon the phase transition, as in the cases of Pt$_2$(*n*-PrCS$_2$)$_4$I and Pt$_2$(*n*-BuCS$_2$)$_4$I.

Introduction

Alkyl groups are not usually considered to play active roles for the functionality of materials and are used as spacers to adjust the spatial arrangement of functional groups in material designs. From the viewpoint of entropy, however, they are unique due to their flexibility:[1] The "potential capacity" of entropy amounts to ca. 10 J K^{-1} (mol of CH$_2$)$^{-1}$, as deduced from the entropy of fusion of *n*-alkanes.[2]

Recently, we have shown that long alkyl chains serve as an "entropy reservoir" in liquid crystalline systems.[3,4] The inversion in the thermal phase sequence was reasonably explained by assuming the entropy transfer between alkyl chains and molecular cores: The phase having large entropy in the alkyl chain appears at high temperatures in a long-chain compound, and vice versa.

Similar entropy transfer was also identified in a quite different system, halogen-bridged one-dimensional (1D) binuclear metal complexes, the so-called MMX chains. They have recently attracted much interest because of possible varieties of their electronic states such as metal, Mott−Hubbard insulator, bond-order wave (BOW), X-CDW (charge-density wave on X), M-CDW, X-SDW (spin-density wave on X), M-SDW, and spin-bond-order wave (SBOW), etc.[5,6] Systems where the entropy

transfer was observed are Pt$_2$(*n*-PrCS$_2$)$_4$I (*n*-Pr, *n*-propyl)[7] and Pt$_2$(*n*-BuCS$_2$)$_4$I (*n*-Bu, *n*-butyl).[8] Although the alkyl groups certainly serve as the entropy reservoir there, the amount of the reserved entropy is only k_B ln 2 per group. This means that a group has only two configurations with the perfect motional correlation within a group and that another group may play the same role. To demonstrate the generality of the function of alkyl chains to act as an entropy reservoir, it is desirable to find a system that exhibits the transfer of a large amount of entropy. We therefore decided to extend the study to the title compound, Pt$_2$(*n*-PenCS$_2$)$_4$I (*n*-Pen, *n*-pentyl).

The MMX complexes expressed as M$_2$(RCS$_2$)$_4$I (R, alkyl chain) have been studied from interest in the effect of interchain interaction on the electronic properties.[9−15] Besides, the elongation of the alkyl chains introduces motional degrees of freedom in the system, which is also of current interest.[16−19] In previous papers,[7,8] the model of the structural disorder was established through the analysis of the entropy of phase transitions for Pt$_2$-(*n*-PrCS$_2$)$_4$I and Pt$_2$(*n*-BuCS$_2$)$_4$I, and thereby the change in entropy assignable to the electronic/magnetic degrees of freedom was determined. The importance of the motional degrees of freedom was also pointed out for the electronic properties.

For Pt$_2$(*n*-PenCS$_2$)$_4$I, three phases have been known through the electrical transport and the magnetic studies, and the structure of the room-temperature (RT) phase of the as-prepared crystal has been determined by single-crystal X-ray analysis.[13,15] The −Pt−Pt−I− quasi-1D chain is along the *c*-axis. For the RT phase, the crystal structure was determined at 273 K, as shown in Figure 1. The *c*-axis has a periodicity of 3 in a unit of −Pt−Pt−I−. This periodicity involves the structural disorder concerning the dithiocarboxylato groups and the alkyl chains belonging to only the central complex in a unit cell length, as similarly encountered in Pt$_2$(*n*-PrCS$_2$)$_4$I and Pt$_2$(*n*-BuCS$_2$)$_4$I.[10,12]

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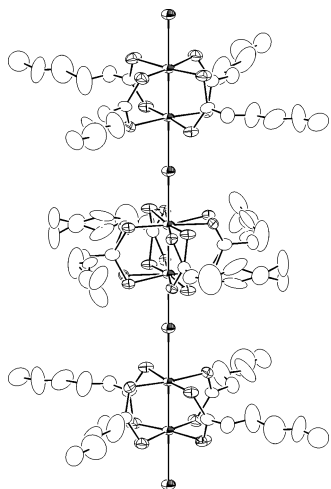
Figure 1. Molecular structure of $Pt_2(n\text{-PenCS}_2)_4I$ of the room-temperature phase at 273 K.[13]

The dithiocarboxylato groups belonging to the two ordered complexes are twisted to the right or the left. That is, the structure is represented as a sequence of -right-disorder-left-. At room temperature, the electrical conductivity of $Pt_2(n\text{-PenCS}_2)_4I$ is ca. 0.84 S cm^{-1}, suggesting the metallic nature of the complex. The minimum in the temperature dependence of the electric resistivity around 235 K is considered to be due to a metal−insulator transition.

On cooling, the complex undergoes a phase transition around 203 K, below which the resistivity strongly depends on temperature. Beside the Bragg reflection corresponding to periodicity 3 (in the unit of −Pt−Pt−I−) along the MMX chain observed in the RT phase, the superlattice reflections corresponding to the periodicity 2 appear, suggesting that the true periodicity of the crystal may be 6. The magnetic susceptibility abruptly drops to the level of the diamagnetic contribution at the transition. This behavior is consistent with the period of even multiple in the unit of −Pt−Pt−I− along the *c*-axis. The electronic structure may be expressed as $-Pt^{2+}-Pt^{3+}-I-Pt^{3+}-Pt^{2+}-I-$ or $-Pt^{2+}-Pt^{2+}-I-Pt^{3+}-Pt^{3+}-I-$. The spins on the adjacent Pt^{3+} are antiferromagnetically coupled strongly, resulting in a nonmagnetic state. That is, this transition seemingly has a character of a spin−Peierls transition concerning lattice distortion and magnetism.[13,15] In these aspects, this transition is quite similar to the MT−RT phase transition (MT, middle temperature) in $Pt_2(n\text{-BuCS}_2)_4I$.[7,12]

On heating the RT phase, the resistivity and thermoelectric power exhibit a jump around 320 K due to a phase transition. The period of the 1D chain of this high-temperature (HT) phase is unchanged across this transition. No transformation from the HT phase to the RT phase has been reported in the results of resistivity.

In the present work, the heat capacity of $Pt_2(n\text{-PenCS}_2)_4I$ was measured by adiabatic calorimetry to characterize the phase transitions detected in the electrical transport and magnetic studies. The transfer of a large amount of entropy was identified at the phase transition from the RT phase to the HT phase. The phase behavior and thermodynamic stability of the "supercooled" HT phase are also discussed.

Experimental Section

The sample synthesized similarly to MMXs with shorter chains[9] was sealed in a gold-plated copper calorimeter vessel with helium gas under atmospheric pressure for adiabatic
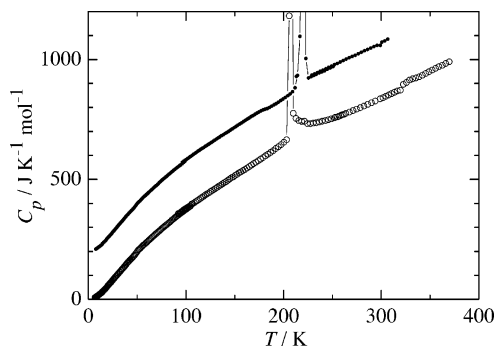
Figure 2. Measured molar heat capacity of $Pt_2(n\text{-PenCS}_2)_4I$. Open circle, measured after initial cooling from room temperature; closed circle, obtained for the sample once heated above 324 K. The closed circles are shifted vertically by 200 J K^{-1} mol^{-1} for clarity.

calorimetry. The mass of the sample loaded was 1.4290 g (1.2845 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.[20] Thermal equilibrium inside the vessel was attained within a normal time (1−10 min depending on temperature) after energy input was turned off, outside the vicinity of first-order phase transitions. The sample contributed to heat capacity by 11% of the total heat capacity including that of the vessel at 50 K, 9% at 100 K, 11% at 200 K, 13% at 300 K, and 14% at 370 K.

Results

The heat capacity of $Pt_2(n\text{-PenCS}_2)_4I$ was measured between 6 and 370 K by adiabatic calorimetry. Typical results are shown in Figure 2, where the data obtained in two series of measurements are plotted by different symbols; open circles are the data measured after initial cooling from room temperature, while closed circles are obtained for the sample once heated above 324 K.

The measurement below room temperature was done first. Three anomalies around 207, 220, and 324 K were observed in the temperature dependence of the heat capacity, while no anomaly was detected by adiabatic calorimetry around 240 K, where a metal−insulator transition is expected.

A sharp thermal anomaly was observed around 207 K, which is reasonably close to the transition temperature detected in the electrical transport and magnetic studies.[13,15] In the transition region the measurements were repeated four times to determine the transition temperature. The temperature of the transition was determined as 207.4 ± 0.2 K. The data around this transition are shown in Figure 3. The data plotted by circles and squares were obtained in a measurement starting from 92.3 and 195.7 K in the heating direction, respectively, whereas the data shown by crosses were from 206.2 K, which is 1 K below the transition temperature. In the latter, the thermal anomaly is absent. The observed supercooling clearly indicates that the phase transition is of the first order.

A small thermal anomaly was detected around 220 K (Figure 4). This anomaly is also of the first order as deduced from possible supercooling. The enthalpy and entropy corresponding to this anomaly were estimated as about 31 J mol^{-1} and 0.14 J K^{-1} mol^{-1}, respectively. The temperature of this anomaly is the same as that of the phase transition around 220 K occurring in the measurement after cooling from 370 K (Figure 2). The details of the phase transition at 220 K will be described later. Considering that the sample used here consists of many small

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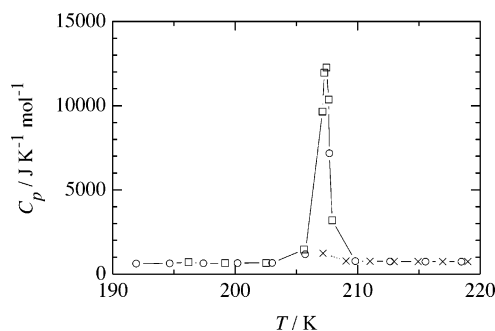
Figure 3. Molar heat capacity of the as-prepared $Pt_2(n\text{-}PenCS_2)_4I$ in the LT−RT phase transition region. Open circle, data obtained after cooling to 92 K; open square, data obtained after cooling to 196 K; cross, data obtained after cooling to 206.2 K.
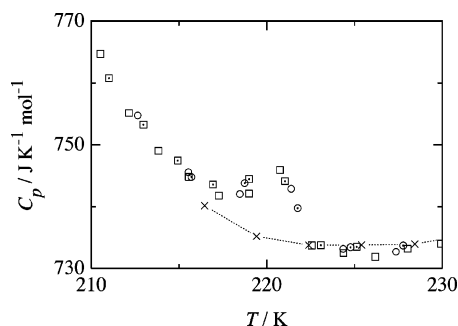

Figure 4. Molar heat capacity of the as-prepared $Pt_2(n\text{-}PenCS_2)_4I$ around 220 K. Open circles and open squares with and without dot, data obtained after cooling below 206.2 K; cross, data obtained after cooling to 214.9 K.
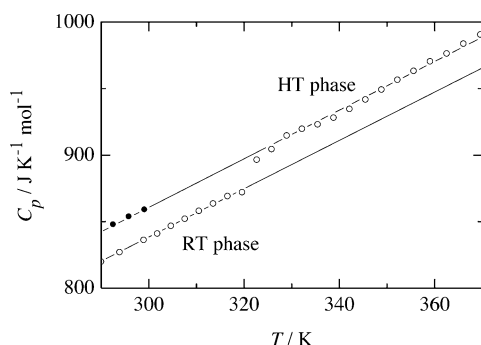

Figure 5. Molar heat capacity of the as-prepared $Pt_2(n\text{-}PenCS_2)_4I$ in the RT−HT phase transition region. Open circle, measured after initial cooling from room temperature; closed circle, obtained for the sample once heated above 324 K.

single crystals, it is reasonable to attribute this anomaly to the phase transition at 220 K of the other phase. Under this assumption, the portion of the sample transformed to the HT phase prior to the calorimetric experiment is estimated as about 0.3% from the magnitude of the anomalies. After correcting for the presence of a small amount of the other phase, the enthalpy and entropy of transitions at 207.4 K were determined as 10.19 ± 0.06 kJ mol^{-1} and 49.1 ± 0.2 J K^{-1} mol^{-1}, respectively.

On heating the RT phase from room temperature, a jump in heat capacity was observed around 324 K. The data around this transition are shown in Figure 5, where the data obtained in two series of measurement are plotted by different symbols; open circles are the data measured after initial cooling from room temperature, while closed circles are the data obtained for the sample once heated above 324 K. This jump is attributed to the phase transition from the RT phase to the HT phase. Neither manifestation of a latent heat nor unusual relaxation
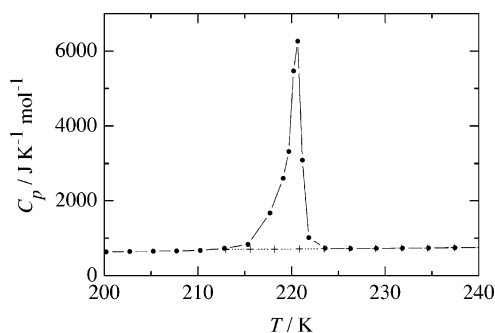
Figure 6. Molar heat capacity of $Pt_2(n\text{-}PenCS_2)_4I$ once heated to 370 K in the MT′−HT phase transition region. Closed circle, data obtained after cooling to 191.3 K; plus sign, data obtained after cooling to 211.7 K.
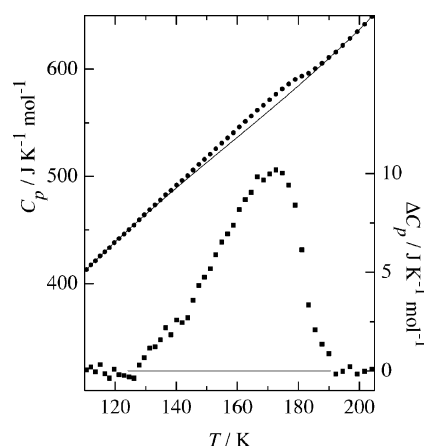
Figure 7. LT′−MT′ phase transition of $Pt_2(n\text{-}PenCS_2)_4I$: molar heat capacity (closed circle) and assumed base line (solid curve) referring to the left axis and excess heat capacities (closed square) referring to the right axis.

typical of a glass transition were encountered. The order of this anomaly is seemingly of the second order according to the classification scheme by Ehrenfest. The upper bounds of the enthalpy and entropy of transition are estimated as about 70 J mol^{-1} and 0.2 J K^{-1} mol^{-1}, respectively, on the basis of the jump in heat capacity and the temperature increment in the measurement. The HT phase that once appeared above 324 K never returns to the RT and/or LT phases even with cooling to liquid helium temperature as indicated by the data plotted by closed circles.

Heat capacity measurements were performed from 6 K for the specimen cooled from 370 K. A sharp heat capacity peak was detected around 220 K on heating, as shown in Figure 6. In this transition region, the measurements were repeated several times to determine the transition temperature. The temperature of the transition was determined as 220.5 ± 0.5 K. The data plotted by closed circles in Figure 6 were obtained in a measurement starting from 191.3 K in the heating direction, whereas the data shown by plus signs are from 211.7 K, which is 9 K below the transition temperature. The observed supercooling clearly shows the phase transition is of the first order. The enthalpy and entropy of transition are determined as 11.56 ± 0.01 kJ mol^{-1} and 52.4 ± 0.2 J K^{-1} mol^{-1}, respectively. The phase below this phase transition is designated as the MT′ phase hereafter. A small thermal anomaly was also detected at 173 K as seen in the upper part of Figure 7. The anomaly has a large tail on the low-temperature side down to about 120 K. Since no latent heat was detected, this anomaly is attributed to a higher-order phase transition. The phase below this anomaly is designated as the LT′ phase from now on. To see the

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magnitude and the shape of the anomaly around 173 K, a normal heat capacity was assumed as a smooth interpolating curve between 110 and 205 K. In practice, the base line was approximated by a cubic polynomial as drawn by a solid curve in Figure 7. The excess heat capacity was then separated by subtracting the normal portion from the observed data and is shown in the lower part of Figure 7. The shape of the heat capacity anomaly is of a typical second-order transition of a mean-field type with small fluctuations. The integration of the excess heat capacity yields the excess enthalpy and entropy as about 360 J mol^{-1} and 2.2 J K^{-1} mol^{-1}, respectively.

Discussion

Thermodynamic Stability of the Phases. Prior to the discussion about the entropy transfer, thermodynamic assessment on the phase sequence should be considered. This concerns the second-order phase transition at 324 K and its monotropic nature.

Although the presence of a very small latent heat (<70 J mol^{-1}) cannot be ruled out, the results depicted in Figure 5 show the phase transition at 324 K is apparently of second order after Ehrenfest. The HT phase once appeared above 324 K never returns to the initial phase, even with cooling to a liquid helium temperature as shown by closed circles in Figure 5. This observation clearly implies the transition is classified as a transition of the first kind after Landau.[21] That is, the observed phase transition is a second-order transition classified as that of the first kind.

Standard enthalpies, entropies, and Gibbs energies are calculated from the experimental heat capacity data for Pt$_2$(n-PenCS$_2$)$_4$I. Small contributions below 6 K are estimated by smooth extrapolation from the high-temperature side. Although two phase sequences are possible, the specimens experiencing different thermal histories are related to each other through the phase transition at 324 K. The LT′ phase is chosen as the reference state, according to the resultant thermodynamic stability. The enthalpy and entropy of the LT′ phase are accordingly 0 J mol^{-1} and 0 J K^{-1} mol^{-1}, respectively, at 0 K. Molar enthalpy and entropy of the LT phase are calculated as about 1.9 kJ mol^{-1} and 4.7 J K^{-1} mol^{-1}, respectively, at 0 K in comparison with those at 324 K (1795 kJ mol^{-1} and 1107 J K^{-1} mol^{-1}), where the two samples are interrelated. The relative magnitude of those of the LT phase is too small to deduce a definite conclusion on the relative stability of the LT and LT′ phase at 0 K and whether the third law does hold for the LT′ phase though the absence of glass transitions implies this.

Although the difference in thermodynamic stability at low temperatures is very small as shown above, a definite comparison is possible if attention is payed to the vicinity of the phase transition at 324 K. The differences between the RT phase and the HT phase are plotted in Figure 8. Here, the definition of quantities is, for example, $\Delta G = G_{RT} - G_{HT}$. The differences are zero at the transition temperature (324 K). ΔG is positive both above and below 324 K whereas ΔH and ΔS change their signs between positive and negative. The positive ΔG shows that the RT phase is not stable but metastable even below 324 K. The phase transition observed here is therefore that from a metastable (RT) phase to a stable (HT) phase. This is fully consistent with the monotropic nature of the RT → HT phase transition.

There remains a point to be considered concerning the RT−HT phase transition. That is, why does the phase transition occur at a fixed temperature (324 K) in resistivity measurements.[13] The RT phase is always metastable according to Figure 8. A
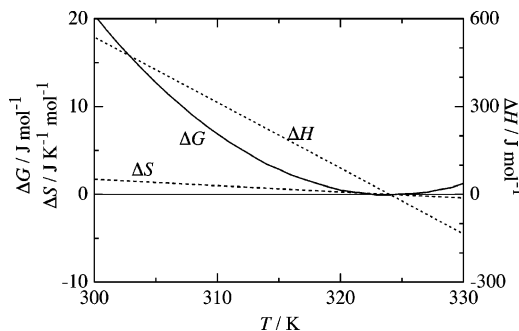
Figure 8. Differences in enthalpy (ΔH), entropy (ΔS), and Gibbs energy (ΔG) of Pt$_2$(n-PenCS$_2$)$_4$I in the vicinity of the RT−HT phase transition at 324 K. As for the definition of the differences, for example, $\Delta G = G_{RT} - G_{HT}$.

possible explanation is as follows: The RT phase is stable in only a limited temperature range below 324 K. Using the maximum bound of the enthalpy of transition (70 J mol^{-1}) and the difference in heat capacity (ca. 23 J K^{-1} mol^{-1}), the stable temperature range of the RT phase is tentatively estimated as 321−324 K. In this case, the stable phase sequence of Pt$_2$(n-PenCS$_2$)$_4$I will be HT phase → RT phase → HT phase on heating separated by two first-order phase transitions with small enthalpy of transitions (<70 J mol^{-1} for both). Anyway, the RT phase remains metastable at room temperature. This is why the LT′ phase was chosen as the reference state at a low temperature.

Entropy Transfer at the Phase Transition of the as-Prepared Sample. The as-prepared Pt$_2$(n-PenCS$_2$)$_4$I shows the phase sequence of LT phase−RT phase−HT phase on heating from the lowest temperature. The phase transition from the RT phase to the HT phase is monotropic and never occurs in the reverse direction as described in the previous section.

The molecular structure in the RT phase of Pt$_2$(n-PenCS$_2$)$_4$I have been determined by single-crystal X-ray experiments,[13] while it is not for the LT and the HT phase. Structural disorder was reported for the RT phase. The reported pattern of structural disorder for the RT phase in Pt$_2$(n-PenCS$_2$)$_4$I is similar to that in Pt$_2$(n-PrCS$_2$)$_4$I and Pt$_2$(n-BuCS$_2$)$_4$I.[10,12]

Despite such similarities in structural disorder, the corresponding entropy of transition is largely different as compared in Table 1. For the phase transitions in Pt$_2$(n-PrCS$_2$)$_4$I and Pt$_2$-(n-BuCS$_2$)$_4$I,[7,8] the entropies of transitions are well-accounted for by the statistical model of disorder and electronic contributions. The crucial assumption of this model of disorder is that the entropy reserved in alkyl groups in the RT phase is transferred to the dithiocarboxylato groups when the RT−HT phase transition occurs.

The entropy gain at the LT−RT transition of Pt$_2$(n-PenCS$_2$)$_4$I is really large as follows. The change in magnetic susceptibility around 200 K is similar to that of Pt$_2$(n-BuCS$_2$)$_4$I.[12,13,15] The contribution of the change in electronic state may be expected being ca. 5 J K^{-1} mol^{-1} referring to that in Pt$_2$(n-BuCS$_2$)$_4$I.[8] Supposing independent twist of the dithiocarboxylato groups in two senses (right or left), the entropy gain is calculated as R (ln 2^4)/3 $\approx$ 7.68 J K^{-1} mol^{-1} while recalling that only a complex shows disorder in a tripled period. Since it is hard to imagine other types of disorder for the dithiocarboxylato groups, the rest [36 J K^{-1} mol^{-1} = (49 − 5 − 8) J K^{-1} mol^{-1}] should be assigned to the pentyl chains. If this is distributed only among the chains attached to the disordered dithiocarboxylato groups, the number of microscopic states per chain is calculated as larger than 25 according to Boltzmann's principle. A realistic upper bound of the contribution of the pentyl chains can be obtained

TABLE 1: Comparison of Thermodynamic Quantities of the Phase Transitions with a Model of Structural Disorder

	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[a]	209	2.75	14.6	358	3.50	10.0
Pt$_2$(n-BuCS$_2$)$_4$I[b]	213.5	4.29	20.09	323.5	2.41	7.46
Pt$_2$(n-PenCS$_2$)$_4$I	207.4	10.19	49.1	324	≈0	≈0
model of disorder[a,b]			15.36			7.68

[a] Reference 7. [b] Reference 8.
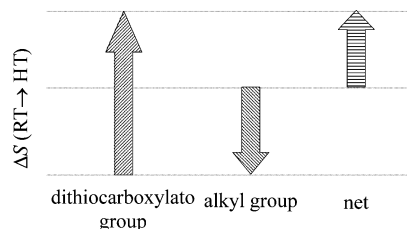
Figure 9. Schematic relationship of entropies of pentyl and dithiocarboxylato groups upon the RT−HT phase transition in Pt$_2$(n-PrCS$_2$)$_4$I, Pt$_2$(n-BuCS$_2$)$_4$I, and Pt$_2$(n-PenCS$_2$)$_4$I.

from the fusion data of alkanes. The fusion data show that the contributions to the entropy of fusion are 10.3 and 3.8 J K^{-1} mol^{-1} for methylene and methyl groups, respectively.[2] Assuming only chains attached to one-third complexes contribute to entropy, the maximum gain is calculated as 60 J K^{-1} mol^{-1}. The experimental entropy of transition corresponds to only 60% of the maximum value. This feature clearly indicates that the alkyl chains can serve as a large entropy reservoir.

In contrast to this, the entropy of the RT−HT transition is effectively null or very small even if present. Since detailed information is unavailable at present, it is hard to construct a model of disorder for the HT phase. In the context of the entropy transfer from the alkyl chains to the dithiocarboxylato groups, however, a phase transition without entropy change is possible because the reserved entropy in the chains (≈36 J K^{-1} mol^{-1}) is much larger than that required for the disordering of all dithiocarboxylato groups (15.4 J K^{-1} mol^{-1} ≈ $R \ln 2^4 - R$ (ln 2^4)/3). By the transfer of entropy of this amount, the number of microscopic states per chain decreases to smaller than 7. It is noted that the number of microscopic states per chain is ca. 2 if all pentyl chains are equivalently disordered, though this assumption is inconsistent with the periodicity of 3 experimentally observed for the HT phase along the MMX chain.[13] This extreme example shows a possibility of moderate disorder in the HT phase (characterized by the number of states per chain being ca. 2) because a small disproportion of entropy distribution can cause the desired periodicity.

The magnitude of entropy of the LT(MT)−RT phase transition and RT−HT phase transitions is reasonably explained for Pt$_2$(n-PrCS$_2$)$_4$I, Pt$_2$(n-BuCS$_2$)$_4$I, and Pt$_2$(n-PenCS$_2$)$_4$I, assuming the transfer of the entropy (disorder) once gained in alkyl chains in the RT phase to the dithiocarboxylato group upon the RT−HT phase transition. The assumed mechanism is schematically shown in Figure 9. In the case of Pt$_2$(n-PenCS$_2$)$_4$I, the net entropy of RT−HT phase transition is effectively null because two contributions compensate for each other. A similar entropy transfer has already been identified as an important mechanism for determining the phase sequence of thermotropic liquid crystals containing isotropic mesophases.[3,4] This clearly indicates that a possible role of alkyl chains as entropy reservoir should be taken into account to understand phase behavior of compounds having long alkyl chains.

Phase Transitions in Stable Phase Sequence. The phase transitions in the "supercooled" Pt$_2$(n-PenCS$_2$)$_4$I are detected

for the first time in this study. There is no detailed information suggesting their mechanisms. The HT phase is metallic and shows a nonvanishing magnetic susceptibility attributable to spins on Pt^{3+}.[13] On the other hand, the integrated calorimetric entropy of the LT′ phase coincides with that of the LT phase within the imprecision of the experiments, as described in a previous section. This means that the LT′ phase is completely ordered in structure and nonmagnetic. Consequently, a metal−insulator transition and a transition to nonmagnetic state are expected between 0 and 324 K on cooling.

Since no information is available now for the physical properties even for the HT phase below room temperature, it is hard to discuss mechanisms of the LT′−MT′ and MT′−HT transitions. The entropy of the MT′−HT phase transition at 220.5 K is as large as 52.4 J K^{-1} mol^{-1}, the most part of which should be attributed to the entropy due to structural disordering as discussed in the previous section. The LT′−MT′ transition at 173 K accompanies only a small thermal anomaly shown in Figure 7. This reminds us of the thermal anomaly in Pt$_2$(n-BuCS$_2$)$_4$I at 114 K.[8] On the other hand, the anomaly around 173 K is too small to be attributed to a spin−Peierls transition, if the contribution to entropy due to the change in electronic state is the same as that estimated for Pt$_2$(n-BuCS$_2$)$_4$I (ca. 5 J K^{-1} mol^{-1}).[8]

Further studies of the electric transport and magnetic properties for MT′ and LT′ phases are strongly desired. Besides the properties of these phases, the study should pursue the point of how the change in aggregation mode modifies the physical properties in two series of phases consisting of the *identical* building blocks.

Conclusion

Heat capacity of a halogen-bridged 1D binuclear metal complex, Pt$_2$(n-PenCS$_2$)$_4$I, was measured by adiabatic calorimetry. A first-order phase transition was observed at 207.4 K when measurement was made after cooling from room temperature. The entropy of transition (49.1 J K^{-1} mol^{-1}) is explained as the sum of the major contribution from structural disordering of dithiocarboxylato and of pentyl groups and the minor electronic/magnetic contribution.

In addition to this, a monotropic phase transition was observed at 324 K. The entropy of transition was essentially null.

The resultant high-temperature phase was easily cooled to low temperatures. This sample showed a different phase sequence in comparison with that of the original sample. A broad anomaly probably due to a higher-order phase transition and a sharp anomaly due to a first-order phase transition were detected at 173 and 220.5 K, respectively. Their entropies of transitions are estimated as 2.2 and 52.4 J K^{-1} mol^{-1}, respectively.

The phase transition at 324 K is seemingly peculiar in its thermodynamic character: second order after Ehrenfest but first kind after Landau. This apparent peculiarity was explained as a phase transition of first order from the metastable phase to the stable phase with a small latent heat. Indeed, the magnitudes

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of heat capacities show that the initial room-temperature phase manifested by the as-prepared sample is metastable at room temperature.

The magnitude of entropies of the LT−RT and RT−HT transitions shows that the mechanism of entropy transfer works also in $Pt_2(n\text{-}PenCS_2)_4I$, similarly to $Pt_2(n\text{-}PrCS_2)_4I$ [7] and $Pt_2(n\text{-}BuCS_2)_4I$,[8] though the entropy reserved in alkyl chains is very large in both the RT and the HT phases of the present compound.

From the interests in quasi-1D electronic systems seen in MMX chain complexes, $Pt_2(n\text{-}PenCS_2)_4I$ offers a possibility to study physical properties of two crystal forms consisting of identical building blocks but with subtle structural differences.

References and Notes

(1) Sorai, M.; Saito, K. *Chem. Rec.* **2003**, *3*, 29.

(2) Sorai, M.; Tsuji, K.; Suga, H.; Seki, S. *Mol. Cryst. Liq. Cryst.* **1980**, *59*, 33.

(3) Sato, A.; Yamamura, Y.; Saito, K.; Sorai, M. *Liq. Cryst.* **1999**, *26*, 1185.

(4) Saito, K.; Shinhara, T.; Nakamoto, T.; Kutsumizu, S.; Yano, S.; Sorai, M. *Phys. Rev. E* **2002**, *65*, 031719.

(5) Yamamoto, S. *Phys. Rev. B* **2001**, *63*, 125124.

(6) Kuwabara, M.; Yonemitsu, K. *J. Phys. Chem. Solids* **2001**, *62*, 435.

(7) Ikeuchi, S.; Saito, K.; Nakazawa, Y.; Mitsumi, M.; Toriumi, K.; Sorai, M. *J. Phys. Chem. B* **2004**, *108*, 387.

(8) Ikeuchi, S.; Saito, K.; Nakazawa, Y.; Sato, A.; Mitsumi, M.; Toriumi, K.; Sorai, M. *Phys. Rev. B* **2002**, *66*, 115110.

(9) Mitsumi, M.; Murase, T.; Kishida, H.; Yoshinari, T.; Ozawa, Y.; Toriumi, K.; Sonoyama, T.; Kitagawa, H.; Mitani, T. *J. Am. Chem. Soc.* **2001**, *123*, 11179.

(10) Mitsumi, M.; Umebayashi, S.; Ozawa, Y.; Toriumi, K.; Kitagawa, H.; Mitani, T. *Chem. Lett.* **2002**, 258.

(11) Mitsumi, M.; Toriumi, K. To be submitted for publication.

(12) Mitsumi, M.; Kitamura, K.; Morinaga, A.; Ozawa, Y.; Kobayashi, M.; Toriumi, K.; Iso, Y.; Kitagawa, H.; Mitani, T. *Angew. Chem., Intl. Ed.* **2002**, *41*, 2767.

(13) Mitsumi, M.; Yamashita, T.; Ozawa, Y.; Toriumi, K. To be submitted for publication.

(14) Ito, H.; Hasegawa, Y.; Tanaka, H.; Kuroda, S.; Mitsumi, M.; Toriumi, K. *J. Phys. Soc. Jpn.* **2003**, *72*, 2149.

(15) Tanaka, H.; Kuroda, S.; Yamashita, T.; Mitsumi, M.; Toriumi, K. *J. Phys. Soc. Jpn.* **2003**, *72*, 2169.

(16) Saito, K.; Akutsu, H.; Sorai, M. *Solid State Commun.* **1999**, *111*, 471.

(17) Akutsu, H.; Saito, K.; Sorai, M. *Phys. Rev. B* **2000**, *61*, 4346.

(18) Saito, K.; Okada, M.; Sato, A.; Sorai, M. *Chem. Phys. Lett.* **2000**, *318*, 75.

(19) Saito, K.; Okada, M.; Akutsu, H.; Sato, A.; Sorai, M. *J. Phys. Chem. B* **2004**, *108*, 1314.

(20) Yamamura, Y.; Saito, K.; Saitoh, H.; Matsuyama, H.; Kikuchi, K.; Ikemoto, I. *J. Phys. Chem. Solids* **1995**, *56*, 107.

(21) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*, 3rd ed., Part 1; Pergamon Press: New York, 1980; Chapter XIV.