PHYSICAL REVIEW B **66**, 115110 (2002)

Calorimetric study of the halogen-bridged mixed-valence binuclear metal chain complex $Pt_2(n\text{-}Bu\mathrm{CS}_2)_4\mathrm{I}$ (Bu=butyl chain)

Satoaki Ikeuchi,[1] Kazuya Saito,[1] Yasuhiro Nakazawa,[1,*] Akane Sato,[1,†] Minoru Mitsumi,[2] Koshiro Toriumi,[2] and Michio Sorai[1]

[1]*Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

[2]*Department of Material Science, Himeji Institute of Technology, Harima Science Park City, Hyogo 678-1297, Japan*

(Received 23 May 2002; published 11 September 2002)

Heat capacity of a halogen-bridged quasi-one-dimensional mixed-valence binuclear metal complex (the so-called MMX chain), $\mathrm{Pt}_2(n\text{-}Bu\mathrm{CS}_2)_4\mathrm{I}$, was measured by adiabatic calorimetry. First-order phase transitions were observed at 213.5 K and 323.5 K. For the former, the enthalpy and entropy of transition were $4.29\ \mathrm{kJ\,mol^{-1}}$ and $20.09\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. Those of the latter were $2.41\ \mathrm{kJ\,mol^{-1}}$ and $7.46\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. Another thermal anomaly probably due to a higher-order phase transition was detected at 114 K. The magnitude of the entropy of transition shows that, upon heating, the butyl chains in one-third complexes in crystalline $\mathrm{Pt}_2(n\text{-}Bu\mathrm{CS}_2)_4\mathrm{I}$ are changed from an ordered state to a disordered state through the phase transition at 213.5 K, and resume the ordered state from this disordered state at 323.5 K. The transition at 213.5 K involves a ‘‘spin-Peierls’’ contribution beyond the structural one.

DOI: 10.1103/PhysRevB.66.115110 PACS number(s): 71.30.+h, 65.40.Gr, 64.60.Cn, 82.60.Fa

I. INTRODUCTION

Quasi-one-dimensional (Q1D) electron systems have provided a variety of interesting electronic, magnetic, and optical properties.[1] Systems extensively studied so far cover transition metal chalcogenides, organic conductors, inorganic and organic polymers, and inorganic complexes such as KCP $[\mathrm{K_2Pt(CN)_4}\cdot X_{0.3}\cdot n\mathrm{H_2O}\ (X=\mathrm{Br\ or\ Cl})]$.

In crystalline KCP, polymeric Pt chains serve as Q1D conduction paths.[1] Due to a ‘‘single-component’’ nature of the chains, their physics is essentially the same as that in many organic conductors such as TTF-TCNQ (TTF=tetrathiafulvalene; TCNQ=tetracyanoquinodimethane). Introduction of other ‘‘components’’ into the 1D path extends the possibility of variation of electronic states.[2–4] Halogen-bridged 1D mononuclear metal complexes, the so-called MX chain, have intensively been investigated in this decade. In MX chains, the half-filled conduction band is made up primarily of an antibonding combination of transition-metal (Md_{z^2}) orbitals and bridging halogen (Xp_z) orbitals. MX chains are insulating due to Mott-Hubbard localization or a spin-density wave (SDW) formation with electronic structure $-M^{3+}-I-$ for $M=\mathrm{Ni}$,[2,3] or due to a charge-density wave (CDW) formation with the electronic structure —M^{2+}—X^--M^{4+}-X^-— for $M=\mathrm{Pt}$ or Pd.[4] Here the relative bond lengths are qualitatively indicated by the length of dashes.

Halogen-bridged 1D mixed-valence binuclear metal complexes, the so-called MMX chain, have recently attracted much interest. In contrast to the MX chains, there exist metal-metal bonds in the MMX chains. This gives possibilities of more varieties of their electronic states such as metal, Mott-Hubbard insulator, bond-order wave, X-CDW (CDW on X), M-CDW, X-SDW, M-SDW, spin bond-order wave (SBOW), etc.[5,6] The half-filled Q1D conduction band is of an antibonding combination of transition-metal (Md_{z^2}) orbitals within a unit cell. Representatives of the MMX compounds having been studied are $A_4[\mathrm{Pt}_2(pop)_4X]\cdot n\mathrm{H_2O}$ ($A=$Li, K,Cs,$\mathrm{NH_4}$; $pop=\mathrm{H_2P_2O_5^{2-}}$, diphosphonato; $X=$Cl, Br, I),[7–13] and $M_2(R\mathrm{CS_2})_4\mathrm{I}$ ($M=$Pt, Ni; $R=$alkyl chain).[14–26] Among them, $\mathrm{Pt_2(CH_3CS_2)_4I}$ [may be written as $\mathrm{Pt}_2(Me\mathrm{CS}_2)_4\mathrm{I}$ because of the name of $\mathrm{CH_3}$ group (methyl group), or as $\mathrm{Pt}_2(dta)_4\mathrm{I}$ because of the name of the ligand (dithioacetato)] attracts wide interests because the metallic state has been found for the first time in MMX chains.[19]

It is widely accepted[20] that sulfur atoms in ligands ($R\mathrm{CS_2}$) enhance the dimensionality of chains in $M_2(R\mathrm{CS_2})_4\mathrm{I}$ through weak van der Waals S-S contacts between neighboring chains. The strength of S-S contacts, and consequently the dimensionality of the electronic system, will be reduced when the alkyl chains (R) in ligands are elongated. Besides, the elongation introduces motional degrees of freedom in the system. Interplay between molecular dynamics and electronic degrees of freedom is also of current interest in organic conductors,[27–29] though the direct interaction between them is ineffective because the time scale of electron motion is quite different from that of molecular dynamics. Indeed, in κ-$\mathrm{(ET)_2Cu[N(CN)_2]Br}$ [ET =bis(ethylenedithio)tetrathiafulvalene] that has the highest superconducting (SC) transition temperature (T_c) under ambient pressure, the freezing of molecular motion strongly affects the SC properties, such as T_c and SC volume.[27,28] Mitsumi and Toriumi[23–26] thus started a systematic study on a homologous series of $M_2(R\mathrm{CS_2})_4\mathrm{I}$ having long chains. The present paper will be concerned with such a Pt compound, $\mathrm{Pt}_2(n\text{-}Bu\mathrm{CS}_2)_4\mathrm{I}$, with the n-butyl chain ($\mathrm{CH_3}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-).

Heat-capacity calorimetry is quite powerful in studying phase transitions resulting from molecular dynamics. Motional degrees of freedom are directly reflected on entropy that is the most significant quantity the heat-capacity calorimetry offers. For example, in $\mathrm{Pt}_2(Me\mathrm{CS}_2)_4\mathrm{I}$, an order-disorder transition of the dithiocarboxylato ligand ($Me\mathrm{CS}_2$)

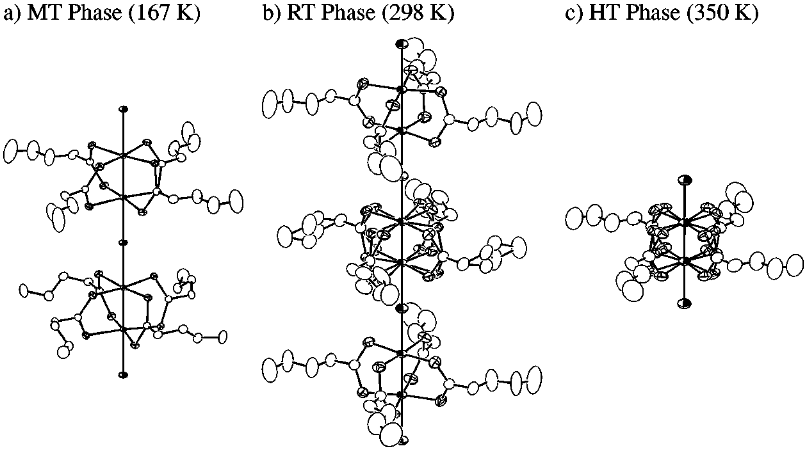

FIG. 1. Molecular structures of $Pt_2(n\text{-}Bu\mathrm{CS}_2)_4I$ of (a) the MT phase at 167 K, (b) the RT phase at 298 K, and (c) the HT phase at 350 K. Only the complexes contained in a lattice period along the chain are shown.

takes place at 373.4 K. Since the entropy of transition ($5.25\ \mathrm{J\,K^{-1}\,mol^{-1}}$) is comparable to $R\ln 2$, it was concluded that four dithiocarboxylato ligands in a formula complex are disordered not independently but in a synchronized way.[22]

For the title compound $Pt_2(n\text{-}Bu\mathrm{CS}_2)_4I$, three phases have been known through the transport and the magnetic studies,[25] and their structures have been determined by the single-crystal x-ray analyses at variable temperatures[25,26] as shown in Fig. 1. The high-temperature (HT) phase [Fig. 1(c)] appearing above ca. 324 K has uniform structure along the 1D chain (the *c* axis of tetragonal system).[26] The uniform structure with an inversion center implies the electronic structure of $-\mathrm{Pt}^{2.5+}-\mathrm{Pt}^{2.5+}-\mathrm{I}^{-}-$. According to this electronic structure, the complex shows high electrical conductivity (ca. $30\ \mathrm{S\,cm^{-1}}$) with weak temperature dependence. The dithiocarboxylato groups (CS_2) show a structural disorder concerning their twist with respect to the Q1D chain as shown in Fig. 1(c). On cooling, the conductivity and thermopower exhibit a jump around 324 K due to a first-order transition. This phase is stable down to 210 K and designated as the room-temperature (RT) phase in the present paper. The crystal structure was determined at 298 K.[25] The *c* axis is tripled as shown in Fig. 1(b) while the electronic state may be expressed as $-\mathrm{Pt}^{2.5+}-\mathrm{Pt}^{2.5+}-\mathrm{I}^{-}-$, as judged from the bond lengths. The structural disorder is detected for the dithiocarboxylato group and the butyl chains belonging to only the center complex in a unit cell length $(3c)$. The conductivity and thermopower have rather weak temperature dependence, suggesting a semimetallic nature of this phase. On further cooling, the complex undergoes a phase transition around 210 K, below which thermopower strongly depends on the temperature, as in insulators. The magnetic susceptibility abruptly drops to the level of the diamagnetic contribution at the transition. This behavior is consistent with a doubled period in the *c* axis (in units of that of the HT phase) [Fig. 1(a)]. The electronic structure may be expressed as —$\mathrm{Pt}^{2+}-\mathrm{Pt}^{3+}$-$\mathrm{I}^{-}$-$\mathrm{Pt}^{3+}$–$\mathrm{Pt}^{2+}$—$\mathrm{I}^{-}$—. The spins on Pt^{3+} are strongly coupled resulting in a nonmagnetic state, that is, this transition seemingly has a character of a spin-Peierls transition concerning lattice distortion and magnetism.[25]

In this work, the heat-capacity of $Pt_2(n\text{-}Bu\mathrm{CS}_2)_4I$ was measured by adiabatic calorimetry to characterize the phase transitions detected in the transport and the magnetic studies. The results are described in detail and the structural disorders detected in structural study are correlated with the entropies of transition. The contribution of a "spin-Peierls" nature to the entropy of transition around 210 K is also discussed.

II. EXPERIMENT

The sample synthesized as described previously[25] was sealed in a gold-plated copper calorimeter vessel with helium gas under atmospheric pressure. The mass of the sample loaded was 1.5198 g (1.4473 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.[30]

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. The sample contributed to heat-capacity by 12% of the total heat-capacity including that of the vessel at 50 K, 10% at 100 K, 11% at 200 K, 13% at 300 K, and 13% at 360 K.

III. RESULTS

The heat-capacity of $Pt_2(n\text{-}Bu\mathrm{CS}_2)_4I$ was measured between 6 and 360 K. Typical results are shown in Fig. 2. Three anomalies can be found in temperature dependence of the heat-capacity, in contrast to the previous study[25] where two first-order transitions were reported to occur.

A sharp thermal anomaly was observed around 213 K, which is reasonably close to the transition temperature detected in the previous studies.[25] In the transition region, the measurements were repeated several times to determine the transition temperature. The temperature of the transition was determined as (213.5 ± 0.5) K. The data around this transition are shown in Fig. 3. The data plotted by open circles were obtained in a measurement starting from 93 K in the

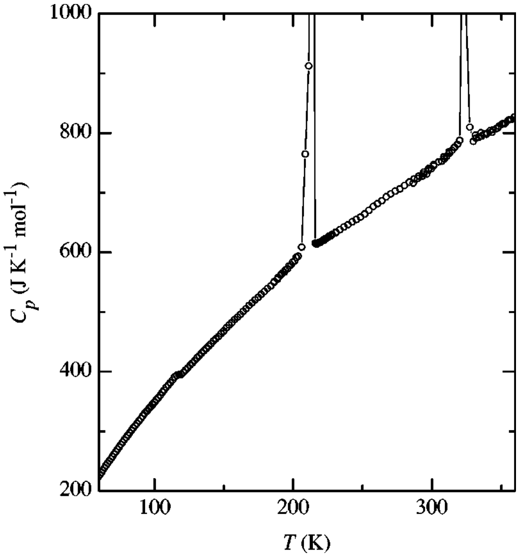

FIG. 2. Measured molar heat-capacity of $Pt_2(n\text{-}Bu CS_2)_4I$ as a function of temperature.

heating direction, whereas the data shown by closed circles from 209.2 K, which is 4 K lower than the transition temperature. No thermal anomaly corresponding to the transition is recognized in this series of measurement. Since the RT phase clearly shows a supercooling phenomenon, the order of this transition is concluded to be a first order. The enthalpy and entropy of the transition were determined as (4.29 ± 0.01) kJ mol^{-1}, and (20.09 ± 0.02) J K^{-1} mol^{-1}, respectively.

At about 324 K, a sharp heat-capacity peak was observed. This anomaly is naturally attributed to the phase transition from the RT phase to the HT phase. In this transition region, the measurements were also repeated to determine the transition temperature. The temperature of the transition was determined as (323.5 ± 1.0) K. The time required for thermal equilibration around the temperature of transition was longer than that of normal region. The order of this phase transition may be regarded as a first order, though no supercooling was observed in spite of some trials. The enthalpy and entropy of transition were (2.41 ± 0.02) kJ mol^{-1} and (7.46 ± 0.08) J K^{-1} mol^{-1}, respectively.

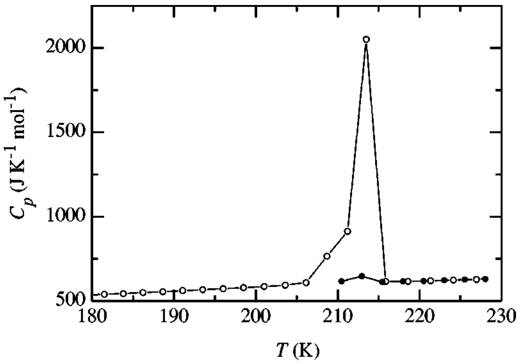

FIG. 3. Molar heat-capacity of $Pt_2(n\text{-}Bu CS_2)_4I$ in the MT-RT phase transition region. Open circle represents data obtained after cooling down to 93 K; closed circle represents data obtained after cooling down to 209.2 K, showing the supercooling of the RT phase.

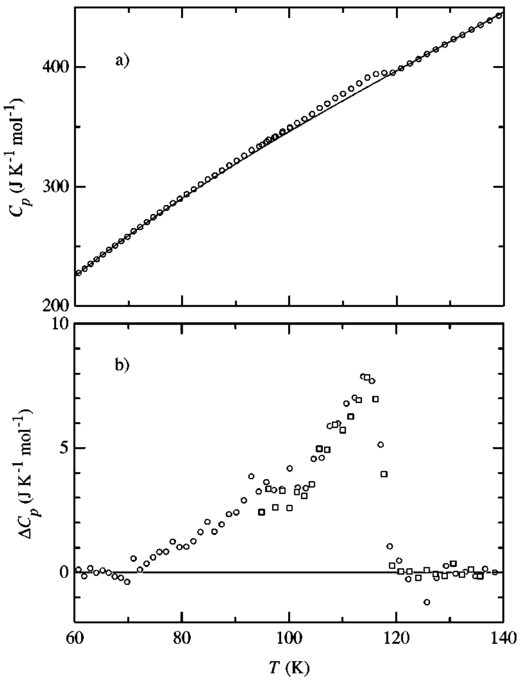

FIG. 4. LT–MT phase transition of $Pt_2(n\text{-}Bu CS_2)_4I$. Molar heat-capacity (open circle) and assumed baseline (solid curve) (a) and the excess heat capacities in two independent series of measurements (circle and square) (b).

Although there is no report suggesting other phase transitions in $Pt_2(n\text{-}Bu CS_2)_4I$, a small thermal anomaly was detected at 114 K, as seen in Fig. 4(a). The anomaly has a large tail on the low-temperature side down to about 70 K. Since no latent heat was detected, this anomaly is attributed to a higher-order phase transition.

IV. DISCUSSION

A. Phase transition at 114 K

To see the magnitude and the shape of the anomaly around 114 K, a normal heat-capacity was assumed as a smooth interpolating curve between 70 and 120 K. In practice, the baseline was approximated by a cubic polynomial as shown by a solid curve in Fig. 4(a). The excess heat-capacity was then separated by subtracting the normal portion from the observed data, and shown in Fig. 4(b), where the data obtained in two series of measurements are plotted using different symbols. Good coincidence of the two data sets demonstrates good accuracy of the present experiment. The shape of the heat-capacity anomaly is a typical second-order transition of a mean-field type with small fluctuations. The integration of the excess heat-capacity with respect to temperature yields the excess enthalpy and entropy as about 150 J mol^{-1} and 1.4 J K^{-1} mol^{-1}, respectively. The excess entropy of transition is one-fourth of $R \ln 2$, a typical magnitude for an order-disorder transition (see below).

Since, to our knowledge, this is the first report of the presence of this phase transition, there is no information sug-

TABLE I. Entropies expected for possible models of structural disorder in $\mathrm{Pt_2}(n\text{-}Bu\mathrm{CS_2})_4\mathrm{I}$.

Phase	Dithio group	Butyl chain	Symbol	S_{ligand} / $(\mathrm{J\,K^{-1}\,mol^{-1}})$	
LT phase	(Unknown)	(Unknown)			
MT phase	(Ordered)	(Ordered)	OO	0.00	$[=R\ln(1\times1)]$
RT phase	Independent	Independent	II	15.36	$[=\frac{1}{3}R\ln(2^4\times2^4)]$
	Independent	Synchronized	IS	9.60	$[=\frac{1}{3}R\ln(2^4\times2)]$
	Synchronized	Independent	SI	9.60	$[=\frac{1}{3}R\ln(2\times2^4)]$
	Synchronized	Synchronized	SS	3.84	$[=\frac{1}{3}R\ln(2\times2)]$
HT phase	(One conformation)				
	Independent	(Ordered)	IO	23.04	$[=R\ln(2^4\times1)]$
	Synchronized	(Ordered)	SO	5.76	$[=R\ln(2\times1)]$
HT phase	(Two conformations)				
	Independent	Independent	II	46.08	$[=R\ln(2^4\times2^4)]$
	Independent	Synchronized	IS	28.80	$[=R\ln(2^4\times2)]$
	Synchronized	Independent	SI	28.80	$[=R\ln(2\times2^4)]$
	Synchronized	Synchronized	SS	11.52	$[=R\ln(2\times2)]$

gesting its mechanism. Since the complex is already nonmagnetic insulator below the ‘‘spin-Peierls’’ like transition at 213 K,[25] there seems to exist no electronic/magnetic degrees of freedom that may lead to any phase transition. The transition mechanism is therefore likely in lattice degrees of freedom. As far as this is assumed, the smallness of the entropy of transition is consistent with the fact that no structural disorder is detected even above this transition (167 K).[25] The small entropy implies a transition mechanism of displacive type, though no information is available as for actual change in the lattice structure. The phase below this phase transition is designated the low-temperature (LT) phase hereafter.

B. Structural disorder and resultant entropy

The molecular structures in the middle-temperature (MT), RT, and HT phases of $\mathrm{Pt_2}(n\text{-}Bu\mathrm{CS_2})_4\mathrm{I}$ have been determined by single-crystal x-ray experiments,[25,26] while it is not for the LT phase. Structural disorder was reported for the RT and HT phases. Since no manifestation of glass transition was encountered in the present heat-capacity experiments, we assume the structural disorder detected by the x-ray study to be dynamical. That is, the complex possibly attains thermal equilibrium in these three phases. In such a case, the nature of the structural disorder should be clarified in order to discuss the properties of phase transitions as structural disorder contributes to entropy according to Boltzmann's relation, $S=xR\ln n$, where x is the population of disordered complex, n the number of available microstates per formula unit, and R the gas constant.

All –Pt–Pt–I– chains in $\mathrm{Pt_2}(n\text{-}Bu\mathrm{CS_2})_4\mathrm{I}$ are crystallographically equivalent to each other in all phases of which the crystal structures are known. Consequently, consideration on a single chain is sufficient for discussion of disorder and entropy. The known crystal structures of $\mathrm{Pt_2}(n\text{-}Bu\mathrm{CS_2})_4\mathrm{I}$ are reproduced in Fig. 1.[25,26] No structural disorder has been detected for the MT phase [Fig. 1(a)]. The RT phase [Fig. 1(b)] has a lattice periodicity of 3 in the MMX unit. There are two crystallographically independent MMX units with the population 1:2. Whereas two units do not show structural disorder, one unit does. The disorder detected is that the dithiocarboxylato group twists clockwise or counterclockwise with a population 1:1 and the butyl chain apparently has two conformations also with 1:1. On the other hand, the HT phase has a lattice periodicity of 1, showing that all the MMX units are equivalent [Fig. 1(c)]. In the HT phase, the dithiocarboxylato group shows a twofold disorder concerning its twist. The butyl chain is seemingly ordered with slightly large thermal factors, suggesting the possibility of structural disorder with multiple conformations.

Now, we consider the structural entropy of each phase on the basis of the reported crystal structure. This is useful because the correlation of the molecular motion resulting in disorder is enumerated only by using entropy as exemplified for $\mathrm{Pt_2}(Me\mathrm{CS_2})_4\mathrm{I}$.[22] We consider here two limiting cases concerning the motional correlation; synchronized or independent. Also assumed is that the molecular disorders of the dithiocarboxylato group and the attached butyl chain are independent.

We can assume that the entropy due to structural disorder is zero for the MT phase, because no disorder was detected[25] (symbolized as OO after the ordered dithiocarboxylato group and ordered butyl chain). For the RT phase, only one-third of MMX units shows disorder ($x=\frac{1}{3}$).[25] If the dithiocarboxylato groups are independently disordered in two twisting senses (‘‘I’’ for short), their contribution to entropy is thus $\frac{1}{3}R\ln 2^4$, here the power 4 is based on the fact that four dithiocarboxylato groups are coordinated to a MMX unit. On the other hand, if the correlation of twisting motion of the dithiocarboxylato groups in a unit is perfect (‘‘synchronized,’’ ‘‘S’’ for short), the contribution of the disorder to entropy is $\frac{1}{3}R\ln 2$. Similarly, the contribution of the butyl chain is also $\frac{1}{3}R\ln 2^4$ assuming independent motion and $\frac{1}{3}R\ln 2$ assuming synchronized motion. There are four possible combinations of modes of disorder (II, IS, SI, and SS), as summarized in Table I.

TABLE II. Entropies of transitions expected for combinations of models of structural disorder in $\mathrm{Pt}_2(n\text{-}Bu\mathrm{CS}_2)_4\mathrm{I}$. Symbols designating models of disorder are given in Table I.

Case	RT phase	HT phase	$\Delta_{\mathrm{trs}}S(\mathrm{MT}\rightarrow\mathrm{RT})$ $(\mathrm{J\,K^{-1}\,mol^{-1}})$	$\Delta_{\mathrm{trs}}S(\mathrm{RT}\rightarrow\mathrm{HT})$ $(\mathrm{J\,K^{-1}\,mol^{-1}})$
1	II	IO	15.36	7.68
2	IS or SI	IO	9.60	13.44
3	SS	IO	3.84	19.20
4	II	IS or SI	15.36	13.44
5	IS or SI	IS or SI	9.60	19.20
6	SS	IS or SI	3.84	24.96
Observed			20.09	7.46

In the HT phase, all the MMX units show disorder. The dithiocarboxylato group is certainly disordered in two conformations as evidenced by the successful refinement of structure by the split-atom method.[26] On the other hand, the butyl chain may be either ordered or weakly disordered. If the butyl chain is ordered (O), there are two possible situations of mode of structural disorder (IO and SO). We also consider the case of the disordered butyl chain here. The butyl chain is assumed to be disordered between two conformations as the simplest model of disorder. Four combinations (II, IS, SI, and SS) are possible in this case as shown in Table I.

As entropy is a state function, the entropy of transition is to be calculated as the difference in the entropy of each phase. The combined entropy of transitions experimentally determined up to the HT phase is 27.55 $\mathrm{J\,K^{-1}\,mol^{-1}}$. Taking this fact into account, the three patterns (SO,II, and SS) of the entropy of structural disorder for HT phase are not compatible with experiments. For possible combinations, the calculated entropy of transitions are tabulated in Table II together with the experimental ones.

It is apparent that the case 1 is the most favorable in comparison with other cases, that is, the dithiocarboxylato group in both the RT and HT phases and the butyl chain in the RT phase are independently disordered, and the butyl chains in the HT phase are ordered. It is noted that the models discussed have assumed only structural disorder. Other degrees of freedom (such as lattice vibration and electronic/magnetic ores) may contribute to the entropy of transition. Considering Peierls systems[31] undergoing CDW formation, the lattice and the electronic degrees of freedom cannot adjust the magnitude of entropy of transition for other cases, though precise information is not available for this compound.

The RT-HT phase transition at 323.5 K is reported to affect scarcely the electrical and magnetic properties, and is reported to be a phase transition having a purely structural origin.[25,26] This is the reason that the entropy of the transition is reproduced well by the above disorder model.

It is noted that the structural entropies gained by one-third of butyl chains in the RT phase are transferred to the dithiocarboxylato groups through establishing their conformational order upon the RT-HT phase transition (on heating); that is, the butyl chains serve as an entropy reservoir. Similar entropy transfer has recently been recognized in thermotropic liquid crystals.[32,33] The existence of the common phenomena in these quite different systems suggests that serving as an entropy reservoir is a general role played by the alkyl chains for determining thermodynamic stability of matters.

C. Phase transition at 213.5 K

The fact that the periodicities of the MT and RT phases (2 and 3 in the unit of –Pt–Pt–I–) do not have a relation of an integer multiple of each other forces the MT-RT phase transition at 213.5 K to be classified as the first kind according to the phenomenological theory by Landau and Lifshitz.[34] Indeed this phase transition is of the first order, which automatically assigns the phase transition to the first kind. This can readily be understood considering the arrangement of the ordered dithiocarboxylato groups in two phases. They are arranged by repeating –right–left–disordered– in the RT phase whereas ordered alternately (–right–left–) in the MT phase. It is evident that any order of the disordered groups in the RT phase does not fit to the MT phase, and that consequently, the reorientation of the groups already *ordered* in the RT phase is necessary for the transformation from the RT phase to the MT phase.

The entropy of the transition from the MT phase to the RT phase is about 4.7 $\mathrm{J\,K^{-1}\,mol^{-1}}$ larger than the entropy expected for the above model of molecular dynamics. This difference should be attributed to the magnetic and lattice degrees of freedom because this phase transition involves a spin-Peierls nature, below which the compound becomes nonmagnetic.

The complex becomes nonmagnetic upon the phase transition on cooling.[25] If free (noninteracting) spins are created upon the phase transition (on heating), their magnetic entropy contributes by $R\ln 2$ $(\approx 5.8\ \mathrm{J\,K^{-1}\,mol^{-1}})$, which is comparable to the observed difference. This scenario is, however, too naive. The spin susceptibility of free-electron spin paramagnet is calculated as 1.7×10^{-3} $\mathrm{emu\,mol^{-1}}$ at 215 K. On the other hand, the experimental value that Mitsumi *et al.*[25] reported is 3×10^{-5} $\mathrm{emu\,mol^{-1}}$, only 2% of the value expected for free spins. Besides, the experimental susceptibility shows a broad hump around 215 K, in contrast to a monotonous Curie behavior of free spins.

The broad hump in susceptibility suggests the presence of antiferromagnetic interaction between the spins. Considering the chain structure of the complex, we may adopt a Heisenberg chain with antiferomagnetic interaction, which Bonner and Fisher[35] investigated in 1960s. They showed that the susceptibility of the chain exhibits a broad hump. If the temperature of the hump is used to adjust scale, the observed susceptibility and (magnetic) entropy are 5% and 4%, respectively, of that expected from the models of the 1D antiferromagnetic system. Although the properties of the 1D electron system with strong correlation have not been fully explored, it seems impossible to attribute the difference between the experimental entropy and the expected one from the disorder model solely to the spin degrees of freedom.

There is, in principle, an additional contribution beyond the magnetic one because spin-Peierls transitions occur due to strong spin-lattice interaction. In structural phase transition originating in purely structural instability in dielectrics, an excess entropy due to the phase transition is typically of the order of a few $\mathrm{J\,K^{-1}\,mol^{-1}}$,[36–38] comparable to the magnitude of entropy under discussion ($5\ \mathrm{J\,K^{-1}\,mol^{-1}}$). Taking this into account, the assignment of the difference to the spin-Peierls nature of the MT-RT phase transition is consistent.

The entropy change assignable to this spin-Peierls nature does not seem to be rationalized by any existing models. It is, however, interesting that the periodicity of 2 of the MT phase is surely preferred by the electronic system for the diamagnetic ground state whereas the structural ordering can be achieved even for the periodicity of 3 (of the RT phase). This suggests that the periodicity of the MT phase originates in the electronic system. Structural (a kind of order-disorder type) and electronic (a kind of spin-Peielrs transition) changes occur simultaneously at this phase transition. Development of new models incorporating explicitly the coupling between the electronic and the lattice (ligand) degrees of freedom will be a possible way to clarify the issue.

V. CONCLUSION

Heat-capacity of a halogen-bridged quasi-one-dimensional binuclear mixed-valence metal complex $\mathrm{Pt_2}(n\text{-}Bu\mathrm{CS_2})_4\mathrm{I}$ was measured by adiabatic calorimetry. First-order phase transitions were observed at 213.5 K and 323.5 K. While the entropy of transition at 323.5 K ($7.46\ \mathrm{J\,K^{-1}\,mol^{-1}}$) is favorably explained by the structural disorder of ligands, that at 213.5 K ($20.09\ \mathrm{J\,K^{-1}\,mol^{-1}}$) involves an additional ‘‘spin-Peierls’’ contribution (ca. $4.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$) beyond the contribution of the structural disorder. The model of structural disorder to explain the entropies of transition assumes that the butyl chains of one-third complexes exhibit the following sequence of disorder: Order (MT phase below 213.5 K)-disorder (RT phase between 213.5 K and 323.5 K)-order (HT phase above 323.5 K) on heating. A thermal anomaly probably due to a structural phase transition of higher order was discovered at 114 K. The excess enthalpy and entropy were estimated to be about $150\ \mathrm{J\,mol^{-1}}$ and $1.4\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively.

The MMX complex represented as $\mathrm{Pt_2}(R\mathrm{CS_2})_4\mathrm{I}$ complex has the structural degrees of freedom concerning the conformation of the alkyl chains and the orientation of the dithiocarboxylato group. Indeed, the first-order phase transition at 213.5 K of the present complex $\mathrm{Pt_2}(n\text{-}Bu\mathrm{CS_2})_4\mathrm{I}$ accompanies the structural disordering and the change in the electronic state. It is concluded that the various electronic states in the MMX system are affected not only by the electronic properties such as the electron correlation and/or the instability of 1D electron system, but also by the structural degrees of freedom of ligands.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (Grant No. 12023229) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

---

*Present address: Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama, Meguro 152-8850, Tokyo, Japan.

†Present address: Department of Organic Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama, Meguro 152-8850, Tokyo, Japan.

[1] S. Kagoshima, H. Nagasaka, and T. Sambongi, *One-Dimensional Conductors* (Springer-Verlag, Berlin, 1988).

[2] K. Toriumi, Y. Wada, T. Mitani, S. Bandow, M. Yamashita, and Y. Fujii, J. Am. Chem. Soc. **111**, 2341 (1989).

[3] H. Okamoto, Y. Shimada, Y. Oka, A. Chainani, T. Takahashi, H. Kitagawa, T. Mitani, K. Toriumi, K. Inoue, T. Manabe, and M. Yamashita, Phys. Rev. B **54**, 8438 (1996).

[4] J.T. Gammel, A. Saxena, I. Batistic, A.R. Bishop, and S.R. Phillpot, Phys. Rev. B **45**, 6408 (1992).

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

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

[7] C.-M. Che, F.H. Herbstain, W.P. Schaefer, R.E. Marsh, and H.B. Gray, J. Am. Chem. Soc. **105**, 4604 (1983).

[8] L.G. Butler, M.H. Zietlow, C.-M. Che, W.P. Schaefer, S. Sridhar, P.J. Grunthaner, B.I. Swanson, R.J.H. Clark, and H.B. Gray, J. Am. Chem. Soc. **110**, 1155 (1988).

[9] S. Jin, T. Ito, K. Toriumi, and M. Yamashita, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **45**, 1415 (1989).

[10] M. Yamashita and K. Toriumi, Inorg. Chim. Acta **178**, 143 (1990).

[11] T. Mitani, Y. Wada, M. Yamashita, K. Toriumi, A. Kobayashi, and H. Kobayashi, Synth. Met. **64**, 291 (1994).

[12] Y. Wada, T. Furuta, M. Yamashita, and K. Toriumi, Synth. Met. **70**, 1195 (1995).

[13] M. Yamashita, S. Miya, T. Kawashima, T. Manabe, T. Sonoyama, H. Kitagawa, T. Mitani, H. Okamoto, and R. Ikeda, J. Am. Chem. Soc. **121**, 2321 (1999).

[14] C. Bellitto, G. Dessy, and V. Fares, Inorg. Chem. **22**, 444 (1983).

[15] C. Bellitto, G. Dessy, and V. Fares, Inorg. Chem. **24**, 2815 (1985).

[16] M. Yamashita, Y. Wada, K. Toriumi, and T. Mitani, Mol. Cryst. Liq. Cryst. Suppl. Ser. **216**, 207 (1992).

[17] I. Shirotani, A. Kawamura, M. Yamashita, K. Toriumi, H. Kawamura, and T. Yagi, Synth. Met. **64**, 265 (1994).

[18] H. Kitagawa, N. Onodera, J.-S. Ahn, T. Mitani, K. Toriumi, and M. Yamashita, Mol. Cryst. Liq. Cryst. Suppl. Ser. **285**, 311 (1996).

[19] H. Kitagawa, N. Onodera, T. Mitani, K. Toriumi, and M. Yamashita, Synth. Met. **86**, 1931 (1997).

[20] H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukawa, T. Mitani, M. Seto, and Y. Maeda, J. Am. Chem. Soc. **121**, 10068 (1999).

[21] H. Kitagawa, S. Nakagami, and T. Mitani, Synth. Met. **116**, 401 (2001).

[22] Y. Miyazaki, Q. Wang, A. Sato, K. Saito, M. Yamamoto, H. Kitagawa, T. Mitani, and M. Sorai, J. Phys. Chem. B **106**, 197 (2002).

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

[24] M. Mitsumi, S. Umebayashi, Y. Ozawa, K. Toriumi, H. Kitagawa, and T. Mitani, Chem. Lett. **2002**, 258 (2002).
[25] M. Mitsumi, K. Kitamura, A. I. Morinaga, Y. Ozawa, M. Kobayashi, K. Toriumi, Y. Iso, H. Kitagawa, and T. Mitani, Angew. Chem. **41**, 2767 (2002).
[26] M. Mitsumi, Y. Ozawa, and K. Toriumi (unpublished).
[27] K. Saito, H. Akutsu, and M. Sorai, Solid State Commun. **111**, 471 (1999).
[28] H. Akutsu, K. Saito, and M. Sorai, Phys. Rev. B **61**, 4346 (2000).
[29] K. Saito, M. Okada, A. Sato, and M. Sorai, Chem. Phys. Lett. **318**, 75 (2000).
[30] Y. Yamamura, K. Saito, H. Saitoh, H. Matsuyama, K. Kikuchi, and I. Ikemoto, J. Phys. Chem. Solids **56**, 107 (1995).
[31] For example, K. Saito, Y. Yamamura, H. Akutsu, M. Takeda, H. Asaoka, H. Nishikawa, I. Ikemoto, and M. Sorai, J. Phys. Soc. Jpn. **68**, 1277 (1999).
[32] A. Sato, Y. Yamamura, K. Saito, and M. Sorai, Liq. Cryst. **26**, 1185 (1999).
[33] K. Saito, T. Shinhara, T. Nakamoto, S. Kutsumizu, S. Yano, and M. Sorai, Phys. Rev. E **65**, 031719 (2002).
[34] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon Press, New York, 1980), Pt. 1, Chap. XIV.
[35] J.C. Bonner and M.E. Fisher, Phys. Rev. A **135**, A640 (1964).
[36] K. Nomoto, T. Atake, B.K. Chaudhuri, and H. Chihara, J. Phys. Soc. Jpn. **52**, 3475 (1983).
[37] T. Atake, K. Saito, and H. Chihara, Chem. Lett. **1983**, 493 (1983).
[38] K. Saito, Y. Yamamura, H. Saitoh, H. Matsuyama, K. Kikuchi, and I. Ikemoto, Solid State Commun. **87**, 903 (1993).