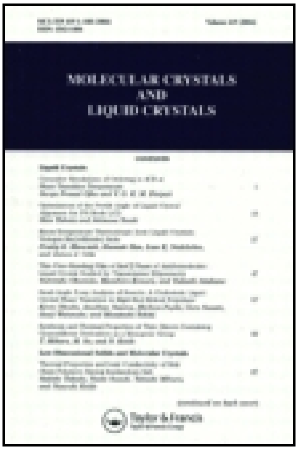

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Transition and Generation Efficiency of Mismatch of Valence-Alternation in the Neutral MX Chain System, $[PtX_2(en)][PtX_4(en)]$ (X = Cl, Br, I)

Nobuyuki Matsushita [a], Akiko Takano [a] & Norimichi Kojima [a]
[a] College of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Meguro, Tokyo, 153, Japan

To cite this article: Nobuyuki Matsushita, Akiko Takano & Norimichi Kojima (1996): Phase Transition and Generation Efficiency of Mismatch of Valence-Alternation in the Neutral MX Chain System, $[PtX_2(en)][PtX_4(en)]$ (X = Cl, Br, I), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 317-322

To link to this article: http://dx.doi.org/10.1080/10587259608030819

Mol. Cryst. Liq. Cryst., 1996, Vol. 285, pp. 317–322

Phase Transition and Generation Efficiency of Mismatch of Valence-Alternation in the Neutral MX Chain System, $[PtX_2(en)][PtX_4(en)]$ (X=Cl, Br, I)

NOBUYUKI MATSUSHITA, AKIKO TAKANO and NORIMICHI KOJIMA
College of Arts and Sciences, The University of Tokyo
Komaba 3-8-1, Meguro, Tokyo 153, Japan

Abstract We have investigated mid-gap absorption bands, their photo-induced absorption effect at various temperatures between liquid helium temperature and room temperature, and crystal structures between 150 K and 300 K in a neutral MX chain system, $[PtX_2(en)][PtX_4(en)]$ (X=Cl, Br, I), which have one-dimensional structure, $\cdots Pt^{II}\cdots X—Pt^{IV}—X\cdots$. Temperature dependence of the intensity of the mid-gap absorption bands and the growth of the photo-induced absorption in $[PtCl_2(en)][PtCl_4(en)]$ show that the generation efficiency of the mismatch of valence-alternation is changed at 200-220 K. Temperature dependence of lattice parameters of $[PtCl_2(en)][PtCl_4(en)]$ shows that the structural phase transition occurs at 220 K from the orthorhombic system to the monoclinic system by cooling. Comparison of the crystal structure between 195 K and 296 K shows that the basic structure does not change at the phase transition. The conformation of the chelate ring of the ethylenediamine is changed from the disordered state to the ordered state at the transition point by cooling. This result suggests that the order-disorder transition of the conformation of the ethylenediamine would be responsible for the generation efficiency of the mismatch of the valence alternation.

INTRODUCTION

One-dimensional mixed-valence platinum complexes (MX chains) are interesting materials on the view point of the non-linear excitations such as kink-solitons and polarons which are the mismatch of the valence alternation. Various kinds of MX chains having counter ions have been investigated for the kink-soliton and the polaron. On the other hand, neutral MX chains without counter ions have scarcely been studied. We expect to control the kink-soliton and the polaron on neutral MX chains by doping electrons or holes into the platinum chain as well as polyacetylene. We previously reported that the neutral MX chains, $[PtX_2(en)][PtX_4(en)]$ (X=Cl, Br, I, en=ethylenediamine) possess mid-gap absorption bands assigned to the mismatch of the valence alternation as the kink-solitons and the polarons.[1] In order to elucidate the kink-soliton and the polaron in the system of the neutral MX chains, we have measured the optical properties of $[PtX_2(en)][PtX_4(en)]$ at various temperatures between liquid helium temperature and room temperature, and performed the single crystal X-ray structure analysis of the Cl-bridged complex between 150 K and room temperature.

EXPERIMENTAL

The absorption spectra of single crystals were measured between 6 K and room temperature with a JASCO CT-100 spectrometer. The measuring method to investigate the photo-induced absorption effect of the mid-gap bands was the same as the method described in our previous paper.[2]

The single crystal X-ray structure analysis of $[PtCl_2(en)][PtCl_4(en)]$ was performed between 150 K and room temperature by using a Rigaku AFC-5S automated four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71069Å) and a variable-temperature apparatus based on a cold nitrogen gas continuous-flow technique. The dimension of the crystal was 0.25×0.18×0.02 mm. Lattice parameters were determined by least-squares fit of 25 reflections ($20.7 \leq 2\theta \leq 29.9°$). The intensity data of X-ray diffraction were collected by θ-2θ scan technique at 195 K and 296 K, and corrected for Lorentz-polarization factors and for absorption correction. Structures were solved by conventional heavy-atom method and refined on *F* by full-matrix least-squares method with anisotropic thermal parameters for non-H atoms, using weighting scheme, $w=[\sigma^2+0.0001|Fo|^2]^{-1}$ for 296 K and $w=[\sigma^2+0.0025|Fo|^2]^{-1}$ for 195 K. Crystal data at 195 K and 296 K are shown in Table I. Programs used were *SHELX* 76[3] and *ORTEP*II[4] on a personal computer NEC PC9801BX/U2.

TABLE I Crystal data of $[PtCl_2(en)][PtCl_4(en)]$

T	195 K	296 K
system	Monoclinic	Orthorhombic
space group	*C2/c*	*Cmcm*
a/Å	5.495(2)	5.518(2)
b/Å	13.517(2)	13.562(2)
c/Å	9.696(2)	9.733(1)
β/°	91.88(2)	
V/Å^3	719.7(3)	728.3(2)
Z	2	2
R	0.074	0.029
Rw	0.088	0.032
parameters	42	29
reflections	922	538

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of $[PtCl_2(en)][PtCl_4(en)]$ at 77 K. The absorption edge (P) is assigned to the intervalence charge-transfer transition from Pt^{II} to Pt^{IV}. The mid-gap absorption bands, A- and B-bands show the photo-induced effect, and should be assigned to the mismatch of the valence alternation as the kink-solitons and the polarons. The intensity of A- and B-bands remarkably decreases between 185 K and 235 K by heating, as shown in Fig. 2. The growth and decay of the intensity by the photo generation extremely change between 200 K and 220 K, as shown in Fig. 3. The photo-induced effect is remarkably strong and the decay time is very long below 210 K. The effect is weak and the time is very short above 210 K. These results show that the generation efficiency of the mismatch of valence-alternation is changed at 200-220 K.

Figure 4 shows the temperature dependence of the lattice parameters of $[PtCl_2(en)][PtCl_4(en)]$ between 150 K and 300 K. This result shows that the structural phase transition occurs at 220 K from the orthorhombic phase to the monoclinic phase by cooling. The parameter β shows a hysteresis between 220 K and 265 K. The *a* axis, along which the Pt—Cl chain lie, shows anomaly at 205 K,

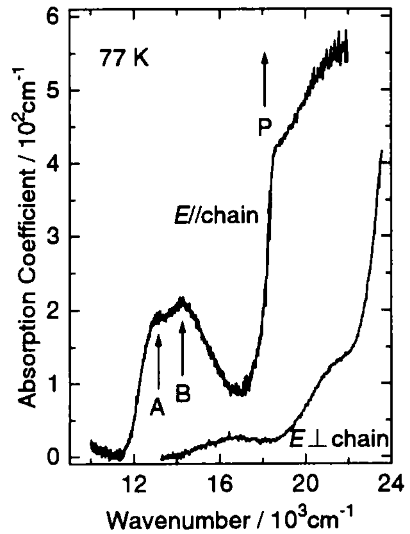

FIGURE 1 Absorption spectra of $[PtCl_2(en)][PtCl_4(en)]$ at 77 K.

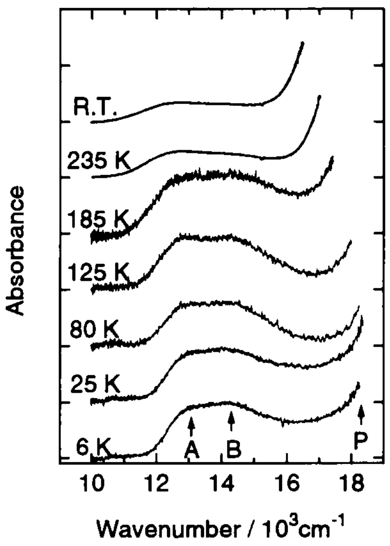

FIGURE 2 Mid-gap absorption bands of $[PtCl_2(en)][PtCl_4(en)]$ at various temperatures.

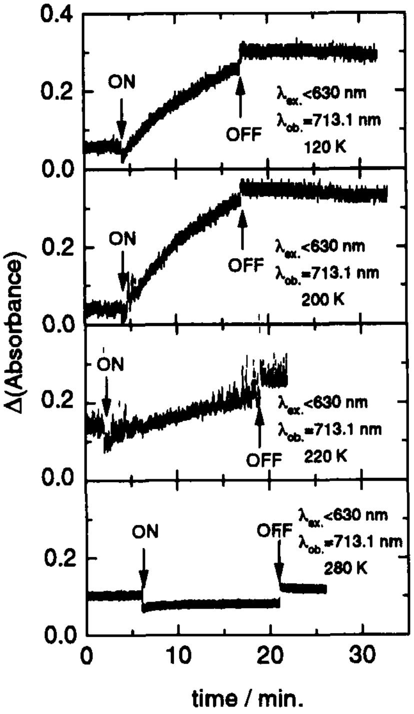

FIGURE 3 Time dependence of the photo-induced absorption in $[PtCl_2(en)][PtCl_4(en)]$ at various temperatures.
"ON" and "OFF" denote that the excitation light (λ<630 nm) turns on and off, respectively.

and moreover dose not depend on temperature below 190 K. On the other hand, the *b* and *c* axes do not show anomaly. Figure 5 shows the perspective views of the crystal structure of $[PtCl_2(en)][PtCl_4(en)]$ looked down along the *a*-axis at 296 K (Fig. 5 (a)) and 195 K (Fig. 5(b)). The crystal structures are almost same at both temperatures, 296 K and 195 K. In the crystal, two dimensional network composed of the Pt columns is constructed by hydrogen-bonding between the in-plane ligand chloride ion on one Pt column and the amine on the adjacent Pt columns, as shown in Fig. 6. The columns lie along the *a* axis. The infinite Pt—Cl chain is slightly bended. The bridging Cl atoms are not at the exact midpoint between the two Pt atoms, and are disordered over two sites close to the midpoint. Thus, each Pt site is occupied by Pt^{II} and Pt^{IV} with different valences in a disordered state.

The basic structure as above mentioned does not change at the phase transition. The conformation of the chelate ring of the ethylenediamine, however, is changed from the disordered state to the ordered state at the transition point by cooling, as

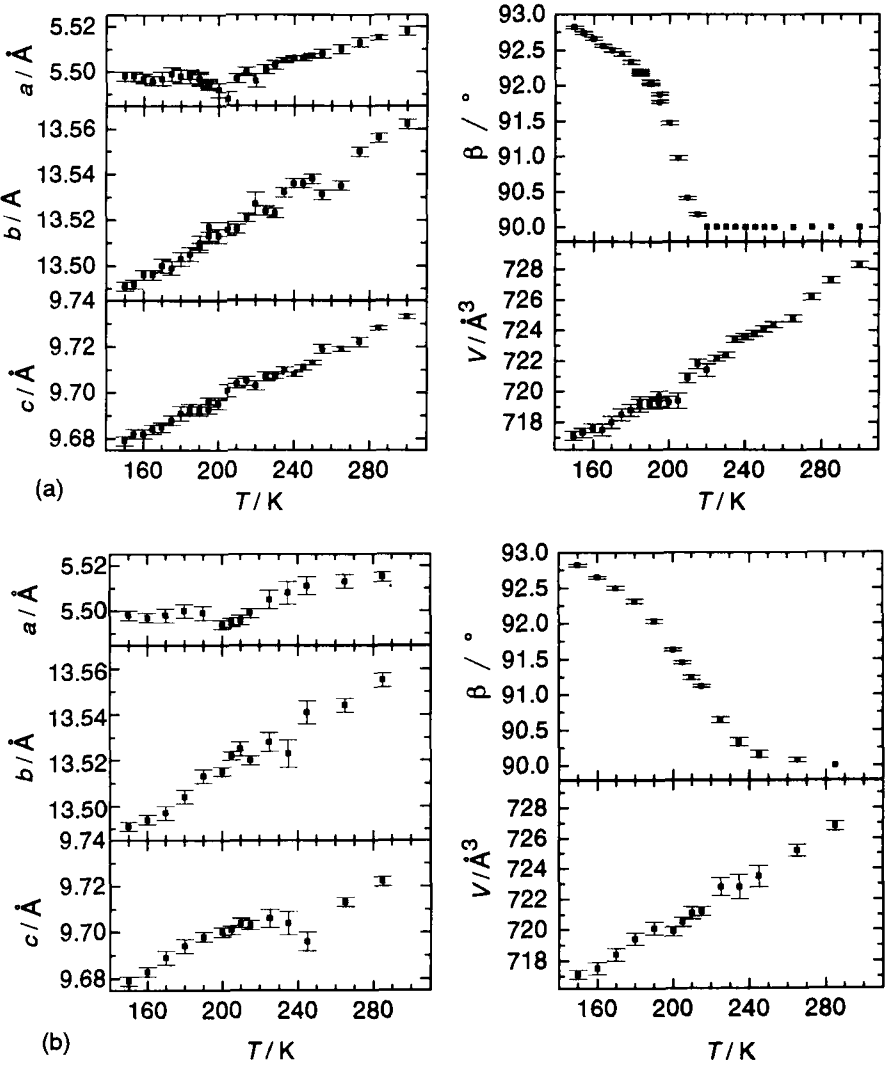

FIGURE 4 Temperature dependence of lattice parameters of $[PtCl_2(en)][PtCl_4(en)]$ in cooling (a) and in heating (b).

shown in Fig. 6. At 296 K, the C atoms of the chelate ring lie on the mirror plane, and have the elongated thermal ellipsoid along the *a* axis. This shows that the chelate rings are disordered over two conformations at 296 K. On the other hand, the each chelate ring is ordered over one conformation at 195 K. This result suggests that the order-disorder transition of the conformation of the ethylenediamine would be responsible for the generation efficiency of the mismatch of the valence alternation.

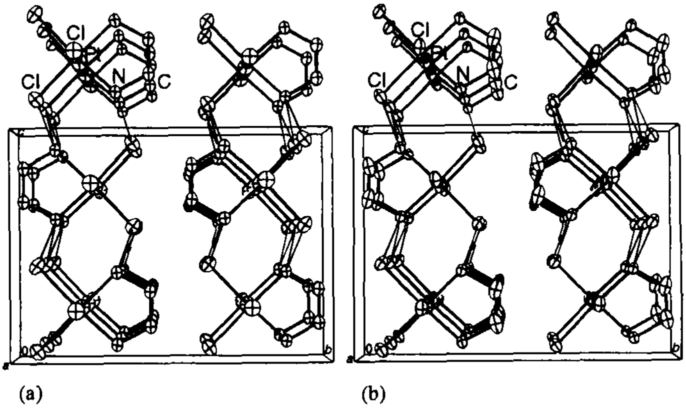

FIGURE 5 Perspective views of the crystal structure of $[PtCl_2(en)][PtCl_4(en)]$ along the *a*-axis at 296 K (a) and 195 K (b).

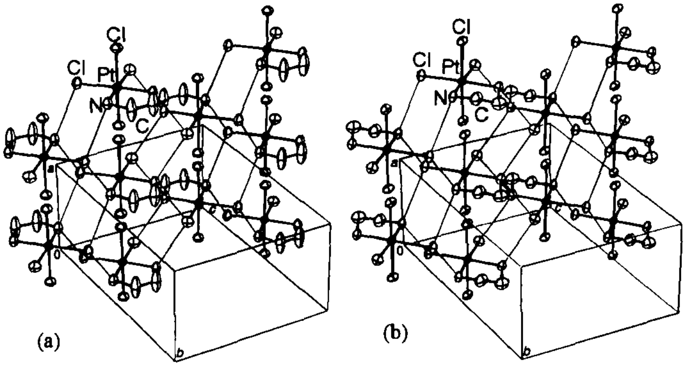

FIGURE 6 Two dimensional network composed of the Pt columns, constructed by hydrogen-bonding at 296 K (a) and 195 K (b).

ACKNOWLEDGEMENTS

One of authors (N.K.) was partly supported by SUMITOMO FOUNDATION and IKETANI FOUNDATION. One of authors (N.M.) was also partly supported by NISSAN SCIENCE FOUNDATION and ASAHI GLASS FOUNDATION.

REFERENCES

1. N. Kojima, S. Maeda, N. Tanaka, and N. Matsushita, *Mol. Cryst. Liq. Cryst.*, 216, 163 (1992)
2. N. Matsushita, N. Kojima, T. Ban, and I. Tsujikawa, *J. Phys. Soc. Jpn.*, 56, 3808 (1987).
3. G. M. Sheldrick, *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England (1976).
4. C. K. Johnson, *ORTEP* II. *Report ORNL*-5138. Oak Ridge National Laboratory, Tennessee, USA (1976).