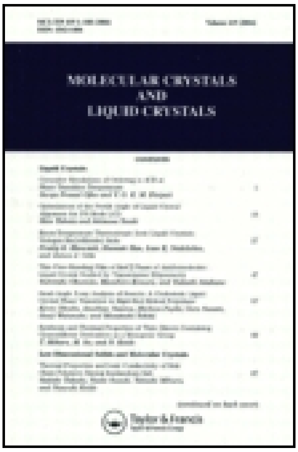

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Mixed-Valence State of a One-Dimensional Platinum Complex with a Counter Ion Having Two Alkyl Chains and its Liquid Crystal Phase

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Mixed-Valence State of a One-Dimensional Platinum Complex with a Counter Ion Having Two Alkyl Chains and its Liquid Crystal Phase

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We have investigated optical property and crystal structure of a one-dimensional halogen-bridged platinum complex (MX chain compound) with a counter ion having two alkyl chains, $[Pt(en)_2][PtCl_2(en)_2]\{(CH_3(CH_2)_7CO_2)_2CH_2CHSO_3\}_4{\cdot}2H_2O$, to elucidate influence of molecular fastener effect of the long alkyl chain on mixed-valence state of the platinum atoms. Thermal-behavior observations of the complex were also performed using a polarizing optical microscope without and with crossed nicols to examine thermal change of the mixed-valence state and appearance of the liquid crystal phase. Consequently, the complex has exhibited that the interaction between the platinum atoms is strengthened and the Pt^{II}-Pt^{IV} distance is shortened by doubling the number of alkyl chains around the platinum complex moieties compared with a corresponding PtCl chain complex with a single alkyl chain counter ion. We have also observed a texture of liquid crystal at about 200 °C.

Keywords: Mixed-Valence State; One-Dimensional Halogen-Bridged Platinum Complex; Long Alkyl Chain; Molecular Fastener Effect; Liquid Crystal Phase

INTRODUCTION

One-dimensional halogen-bridged mixed-valence metal complexes (MX chain compounds), which are typical mixed-valence compounds classified into Class II [1], are very interesting compounds in view of the one-dimensional electron system. A remarkably dichroic strong absorption band attributed to an intervalence charge-transfer (IVCT) transition from "M^{II}" to "M^{IV}" (M=Ni, Pd, Pt) in the mixed-valence state appears as a character of the one-dimensional mixed-valence system. The mixed-valence state depends not only on metal atoms *M* and bridging halogen atoms *X* inside of the *MX* chain, but also on hydrogen bonds between amine ligands *AA* and counter ions *Y* outside of the *MX* chain[2]. The mixed-valence state can be statically controlled by the components of the complexes (*M*, *X*, *AA* and *Y*), but not dynamically controlled. In our recent work[3], a structural investigation of a series of one-dimensional halogen-bridged mixed-valence platinum complexes with single long alkyl chain introduced into the counter ion was performed on the view point of the combination of the mixed-valence state and thermo-dynamical molecular fastener effect reported as a "visible fastener effect" on disk-like metallomesogens[4]. Shortening of the Pt-Pt distance and strengthening of the IVCT interaction in the PtX chain was found in the alkanesulfonates of the one-dimensional platinum complex by the molecular fastener effect. A reversible thermal transition of the mixed-valence state was also observed. The transition was induced by a reversible desorption/adsorption of crystal water, but not by the molecular fastener effect. An interdigitate structure of the alkyl chain in the alkanesulfonates could obstruct the thermo-dynamical behavior of the molecular fastener effect.

In this study, we have investigated the optical property and the crystal structure of a sulfosuccinatedioctyl salt of the chloro-bridged platinum complex, $[Pt(en)_2][PtCl_2(en)_2]\{(CH_3(CH_2)_7CO_2)_2CH_2CHSO_3\}_4{\cdot}2H_2O$ (**1**), in which each counter ion has two alkyl chains, to examine the thermo-dynamical molecular fastener effect on the mixed-valence state due to cancellation of the interdigitate structure of the alkyl chain. In addition, strengthening of the molecular fastener effect applied between platinum complex moieties can be also expected. The structure and property of the present complex has been also compared with related inorganic salts, and the octanesulfonates, $[Pt(en)_2][PtCl_2(en)_2]\{CH_3(CH_2)_7SO_3\}_4{\cdot}2H_2O$ (**2**) and $[Pt(en)_2][PtBr_2(en)_2]\{CH_3(CH_2)_7SO_3\}_4{\cdot}2H_2O$ (**3**).

EXPERIMENTAL

$[Pt(en)_2]Cl_2$, $[PtCl_2(en)_2]Cl_2$ and $\{CH_3(CH_2)_7CO_2\}_2CH_2CHSO_3Na$ were prepared according to the literatures[2,5]. Equimolar $[Pt(en)_2]Cl_2$ and $[PtCl_2(en)_2]Cl_2$ were dissolved in water, and then an ethanol/water solution containing fourfold molar $\{CH_3(CH_2)_7CO_2\}_2CH_2CHSO_3Na$ was added. Metallic lustrous green thin-plate crystals were obtained from concentration of the mixture solution. Single crystals were recrystallized from an ethanol solution on cooling.

Measurement of powder diffuse reflectance spectra was performed using a JASCO V-570 UV/VIS/NIR Spectrometer. A RIGAKU RAXIS-RAPID Imaging Plate diffractometer equipped with graphite-monochromated Mo Kα radiation was used for measurement of X-ray diffraction intensity data. The intensity data were corrected for Lorentz-polarization effects and numerical absorption factors from crystal shape. The structure was solved by a conventional heavy-atom method. The refinement was performed on F^2 by full-matrix least-squares methods with anisotropic thermal parameters except for alkyl group and H atoms. C atoms of alkyl group were refined with isotropic thermal parameters. H atoms were located at geometrically calculated positions with isotropic thermal parameters but were not refined. Programs used were *SHELXS*97[6] for solution, *SHELXL*97[6] for refinement, and *ORTEP*–3[7] for drawing structure, and all the calculations were made on a personal computer. Thermal behavior of the present complex was observed under crossed nicols or under single polarizer using an OLYMPUS BX60 microscope attached with a microscope digital camera and using a LINKAM LK-600FTIR heating stage. The thermal observation was performed with a heating/cooling rate of 2 °C/min between 30 °C and 200 °C. TG and DSC were examined on a TA Instruments TGA2950 and DSC2920 at a scanning rate of 2 °C/min from 30 °C to 250 °C.

RESULTS AND DISCUSSION

The crystal color suggests that the intervalence charge-transfer interaction between the Pt atoms of **1** is much stronger than that of **2**. In powder diffuse reflectance spectra, peak positions of the IVCT bands are 17300 cm^{-1} for **1**, 20700 cm^{-1} for **2**, and 13100 cm^{-1} for **3**, as shown in Figure 1. The IVCT band of **1** is located at a lower energy position than that of **2** in spite of the same chloro-bridged complex, and is considerably closer to that of **3**, which is a different halogen-bridged, bromo-bridged complex. This result shows that the intervalence charge-transfer interaction of **1** is remarkably strong compared with that of **2**. The strengthening of the interaction would be due to doubling the alkyl chain of the counter ion from one to two.

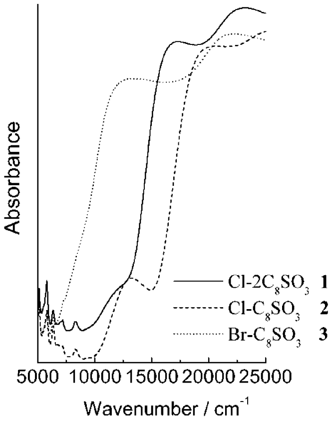

FIGURE 1. Powder diffuse reflectance spectra of **1**~**3**

Crystal data of **1** are shown in Table 1, and crystal packing viewed along the *b* axis is shown in Figure 2. The refinement based on the intensity data at room temperature was converged, but the *R* value is still high. It is may be due largely to a thermal motion of the long alkyl chains which are not in any interdigitate structures at room temperature. Measurements at low temperatures are in progress. The Pt-Cl chains of **1** run along the *b* axis. The crystal packing of **1** is a lamellar structure with the long alkyl chains arranged in parallel. The lamellar structure, especially the arrangement of the inorganic layer part composed of Pt-Cl complex moieties, SO_3 groups of the counter ions and crystal waters, is very similar to those of the alkanesulfonates. The crystal packing of **1** is, however, not an interdigitate structure though that of the alkanesulfonates is an interdigitate structure. Pt^{II}-Pt^{IV}, which corresponds to the cell dimension of *b* axis, Pt^{II}-Cl, and Pt^{IV}-Cl distances of **1** are summarized in Table 2 along with those of **2** for comparison. The Pt-Pt distance of **1** is shorter by about 0.1 Å than that of **2**. The shortening of the Pt-Pt distance would be due to the molecular fastener effect strengthened by doubling the long alkyl chain of the counter ion. This fact supports the result of the powder diffuse reflectance spectra as above mentioned.

TABLE 1 Crystal data of **1**

Triclinic, $P\bar{1}$
$a = 35.396(3)$ Å
$b = 5.2723(7)$ Å
$c = 7.8747(5)$ Å
$\alpha = 89.943(2)°$
$\beta = 94.418(1)°$
$\gamma = 90.080(2)°$
$V = 1465.2(2)$ Å^3
$Z = 1$
D_x /Mg m^{-3} = 1.373
$R\ [F^2 > 2\sigma(F^2)] = 0.2156$

TABLE 2 Pt-Pt and Pt-Cl distances

	1	**2**
$Pt^{II}-Pt^{IV}$ /Å	5.2723(7)	5.3620(1)
$Pt^{II}-Cl$ /Å	2.97(1)	3.041(2)
$Pt^{IV}-Cl$ /Å	2.30(1)	2.323(2)

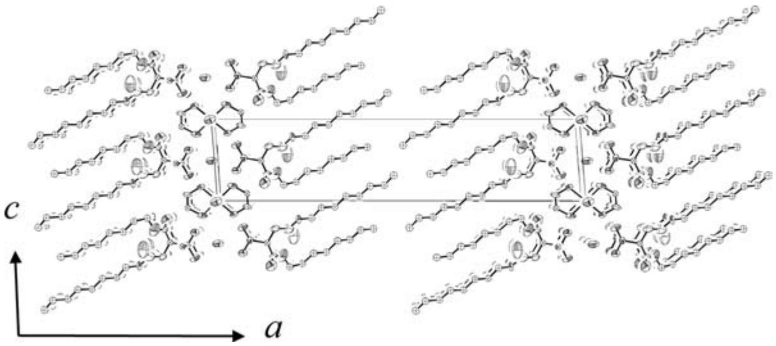

FIGURE 2. Crystal packing of **1** viewed along *b* axis

Observation of thermal behaviors of **1** from 30 ˚C (room temp.) to 200 ˚C exhibits that the crystal has become colorless at around 100 ˚C. The colorless suggests that the mixed-valence state changes to Class I. The original metallic lustrous green color came back after putting them in the room. The reversible change of the crystal color is reproductive. Similar phenomenon was also observed with the alkanesulfonate. TG and DSC data of **1** shows a weight loss around 100 ˚C and an endothermic peak related to the weight loss (Figure 3). The weight loss by 1.4% corresponds to two molecules of water per the chemical formula, which is determined from the single-crystal structure analysis. The color change of **1** would be closely related to desorption of the crystal water. Such color changes related to the desorption of the crystal water are also observed in some inorganic salts of the MX chain compounds. However, the color change of **1** is reversible, while those of the inorganic salts are not reversible. We consider that, in the reversible thermal behavior, a framework structure based on assembled long alkyl chains plays an important role to maintain the Pt-Cl chain structure at the transition between Class II and Class I in spite of the desorption / adsorption of the crystal water. The exothermic peak at 208 ˚C derives

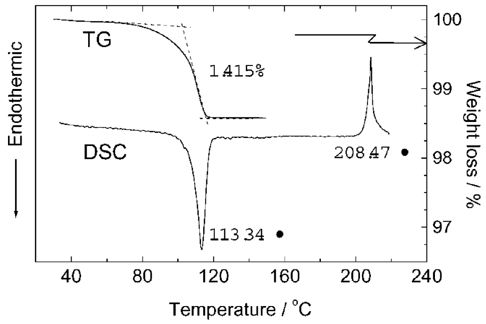

FIGURE 3 TG and DSC of **1**

from decomposition. The crystals of **1** melted above ca. 150 °C, but it was adhesive. At around 200 °C, it turned into a fluid liquid of pale yellow. Such a melting behavior is not observed in the alkanesulfonates. In thermal observations of **1** under crossed nicols of microscope, virgin samples showed no texture of a liquid crystal phase on heating and cooling between room temperature and 200 °C. In the samples experienced in heating and cooling up to 200 °C, however, a neatly oriented domain was observed on cooling process under crossed nicols as shown in Figure 4. The texture is highly reproducible. A fan-like texture as shown in Figure 5 was also observed at 200 °C in the sample experienced in several cycles of heating and cooling.

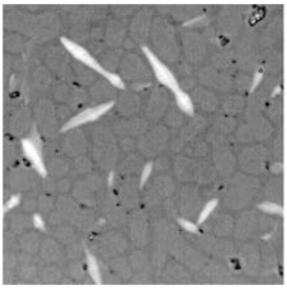

FIGURE 4 Texture observed on cooling from 200 °C

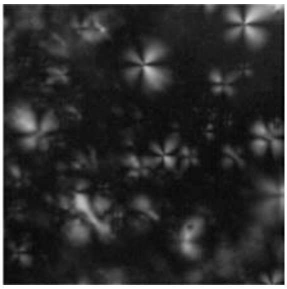

FIGURE 5 Texture observed at 200 °C

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