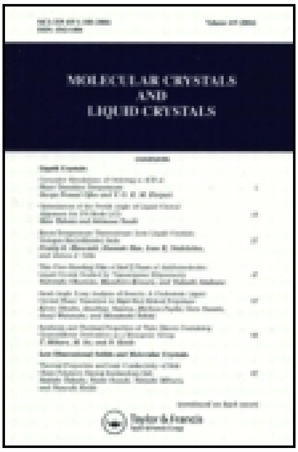

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EPR Study of Photoinduced Defect States in a Quasi-One-Dimensional Halogen-Bridged Platinum Complex

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EPR STUDY OF PHOTOINDUCED DEFECT STATES IN A QUASI-ONE-DIMENSIONAL HALOGEN-BRIDGED PLATINUM COMPLEX.

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Abstract The photo-induced defect states in a quasi-one-dimensional, chlorine-bridged platinum complex (Pt-Cl) were studied by electron paramagnetic resonance (EPR). The EPR spectra consisted of the usual band with the well-known five-fine structure as well as some new bands when the sample at helium temperature was excited by ultra violet light. The new bands were located at about 93 gauss on both sides of the central peak of the usual band when the X band is used. The new bands were less stable than the usual band and completely disappeared at about 30K. These indicate that the photoinduced states consisted of at least two kinds of defects.

INTRODUCTION

The halogen-bridged, mixed-valence transition metal complexes have a doubly degenerate linear chain structure:

$$\ldots\text{-X-M}^{4+}\text{-X-M}^{2+}\text{-X-M}^{4+}\text{-X-M}^{2+}\text{-X-M}^{4+}\text{-}\ldots$$

where X refers to the halogen atom (Cl, Br, I) and M to the transition metal (Ni, Pt, Pd). A single crystal of $[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2Cl_2}](\mathrm{ClO_4})_4$ (abbreviated as Pt-Cl, hereafter), where en is ethylenediamine, was used in this report. In the Pt-Cl chain, the chlorine ions are located, not at the midpoint between the Pt^{2+} and Pt^{4+} ions, but at a point closer to the Pt^{4+} ion. This periodically alternating valence of the Pt ions can be regarded as a charge density wave with a commensurable index of 2. Moreover, the Pt-Cl chain is surrounded by neutral ligands of ethylenediamine. Therefore, the interaction between the different Pt-Cl chains should be fairly small. These facts indicate that the halogen-bridged, mixed-valence transition metal complex qualifies as a good one-dimensional compound with a doubly degenerate structure (CDW). In such a chain, intrinsic defect states (solitons, polarons, bipolarons etc.) are expected to be induced by photoexcitation. In fact photoinduced midgap absorption [1,2] and EPR[3] have been reported and the defects interpreted in terms of the polaron model.[4,5] There is, however, another interpretation, that of a neutral soliton about the EPR spectra.[6] Recently, Okamoto et al.[7] have shown the coexistence of polarons and solitons in Pt-Br crystals. In this report we show detailed EPR experimental results of the photoinduced defect states in Pt-Cl which suggest strongly the existence of two kinds of defect states.

EXPERIMENT

Pt-Cl was synthesized by the method described previously[1] and purified by recrystallization. Single crystals of the orthorhombic and monoclinic phases were grown in an oven at 45°C and in a refrigerator at 5°C, respectively. Samples were held in a liquid-helium transfer cryostat and the temperature was controlled to ±0.3K from 5K to 30K and ±1K in the higher temperature range. The EPR measurement was done by a X band of 1mW power and a 2G modulation amplitude. The crystals were oriented so that the chain axis was perpendicular to the magnetic field. A mercury lamp was used as a light source for the photoexcitation.

RESULTS AND DISCUSSION

Figure 1 shows the photoinduced EPR spectra of a single crystal of Pt-Cl (orthorhombic) at 5K. In the case, (orthorhombic) indicates a crystal grown in the orthorhombic (high temperature) phase and, therefore, a sample at a low temperature changed phases from orthorhombic to monoclinic at 20°C. Light of hν=2.85eV was focussed on the sample face with an intensity of about 1μW/mm^2. The time shown in the figure is the total irradiation time. The spectrum without photoexcitation shows the usual band with a well-known five-fine structure which is always observed at 77K for both the as-grown crystal and with photoexcitation. When the sample at 5K was irradiated by the light, new peaks appeared on both sides of the central peak. These new peaks gave rise to a saturation after 30 min of photolysis. The usual peaks, on the other hand, were continuously enhanced over the 120 min of

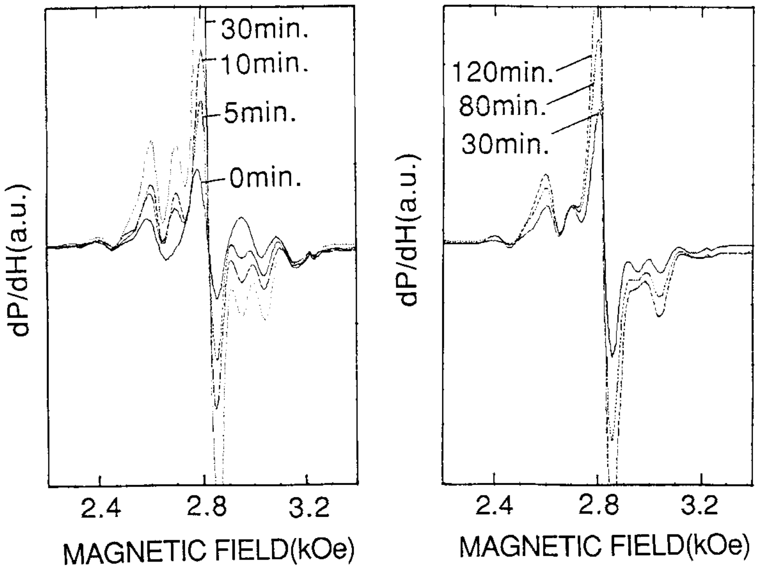

FIGURE 1 The derivative curves of the EPR of a $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ single crystal at 5K as a function of the irradiation time of photoexcitation. The magnetic field was applied perpendicular to the chain axis. Light of 2.84eV with an intensity of about 1μW /mm^2 was used for the photoexcitation.

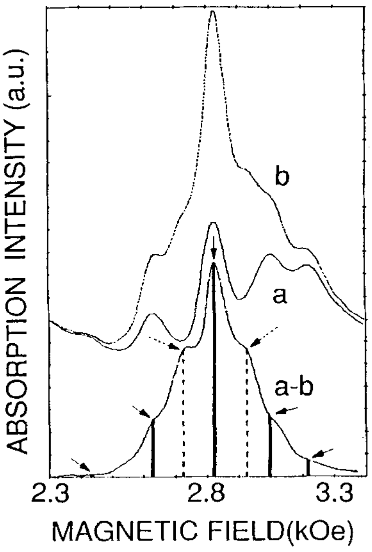

FIGURE 2 Integral curves for the following spectra: (a) after 5 min of photolysis; (b) before the photolysis in Fig.1; and the subtraction of these (a-b). The solid bars indicate the usual bands and the dashed ones the new bands.

photolysis. Figure 2 shows the integral curves for the following EPR spectra: (a) after 5 min of photolysis; (b) before the photolysis in Fig.1; the subtraction of these (a-b). Two new equivalent bands, as well as the usual bands, grow by the photoexcitation. It is not clear whether the new bands accompany the central peak or not because the new bands cannot be separated from the usual bands whereas the integrated curve (b) does not show a well-defined symmetric structure.

Figure 3 shows the annealing effect for the following case: after 120 min of photolysis at 5K, the sample temperature was raised to 20K for 5 min and then cooled to 5K for the EPR measurement. This procedure was repeated for a temperature of 30K. As seen in the figure, the new bands at 30K completely disappear. The newly found defect varies from the well-known photoinduced defect because of the different behavior of the saturation time and thermal instability. If the photo-

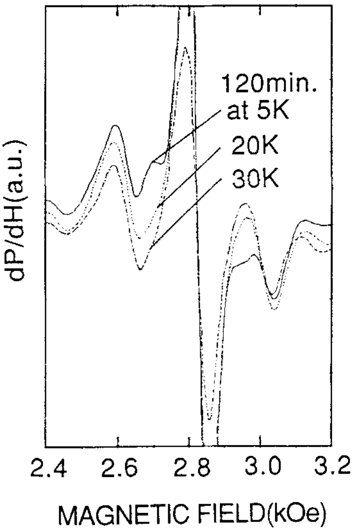

FIGURE 3 The annealing effect of the defect induced by photolysis for 120 min. The EPR spectra were measured at 5K after 5 min at 20K and 30K.

excitation is done at a higher power, the new bands would be buried by the greatly enhanced usual band. The new bands have a low intensity even at low temperatures and disappear at 30K. These are the reasons why the new bands have not been found

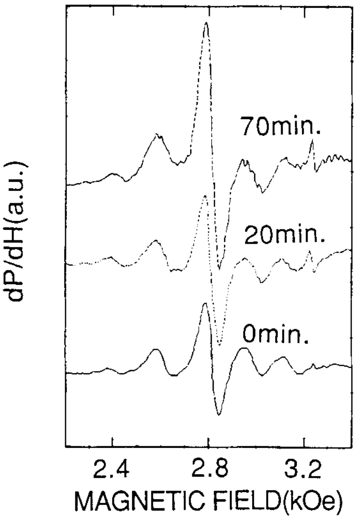

FIGURE 4 Derivative curves of the photoinduced EPR of Pt-Cl (monoclinic) at 5K under the same experimental conditions as Fig.1.

until now. To study the sample dependence of the new bands, we repeated the experiment with a crystal grown in the monoclinic phase which did not change phase during the experimental treatments. Figure 4 indicates that with the Pt-Cl(monoclinic) crystal, the new bands were not produced by photoexcitation. As shown in Fig.3, Pt-Cl (orthorhombic) crystals were found to have two different sorts of photoinduced defect states. Then, it is concluded that the phase change of the crystal is an important factor in the generation of the newly found photoinduced defect states. The defect is very likely located at a chain edge which may be produced occasionally by a breaking of the chain during the process of phase change. This conclusion stems from the fact that a crystal which experiences a phase change becomes very fragile. The EPR spectra of the new defect may consist of a central peak which coincides with the central peak of the usual band and the two symmetric peaks on both sides of the central peak. One candidate for the newly found defect state is an electron localized at a platinum atom on the chain edge.

In conclusion, the newly found band is induced by photoexcitation only at low temperatures and disappear at 30K completely. It is photoinduced only on the samples which have experienced the phase change.

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