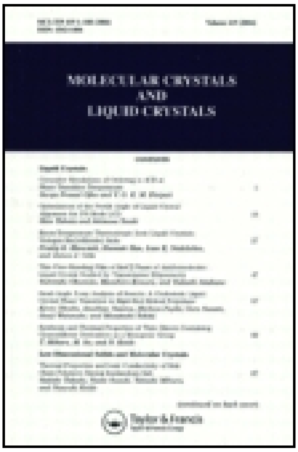

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Optical Studies of MX Chain Complex $[Pt(en)_2]$ $[PtBr_2(en)_2]$ $(SO_4)_2$-$6H_2O$ Under High Pressure

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OPTICAL STUDIES OF MX CHAIN COMPLEX $[Pt(en)_2][PtBr_2(en)_2](SO_4)_2{\cdot}6H_2O$ UNDER HIGH PRESSURE

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Abstract We have measured the absorption and resonance Raman spectra in single crystals of the MX chain complex $[Pt(en)_2][PtBr_2(en)_2](SO_4)_2{\cdot}6H_2O$ in order to study the mixed-valence state, the midgap state and the phase transition under various hydrostatic pressures up to 3.7 GPa at room temperature. Red shifts of both the intervalence charge-transfer absorption edge and the Pt–Br stretching mode Raman peak with increasing pressure show that the electronic state of Pt^{II} and Pt^{IV} in the mixed-valence state approaches that of Pt^{III}. An absorption band appearing above 2.5 GPa and a Raman peak appearing above 1.6 GPa suggest that a new phase coexists at pressures above 1.6 or 2.5 GPa. On the other hand, no enhancement of the optical absorption in the region of the midgap absorption bands (***A***–, ***B***– and ***C***–bands) is observed. This result shows that the midgap state is not generated by applying pressure at room temperature.

INTRODUCTION

Some midgap photo-induced absorption (PA) bands assigned to soliton absorption bands and polaron absorption bands are observed in many one-dimensional halogen-bridged mixed-valence platinum complexes (*MX* chains). It is difficult to assign a PA band to either the soliton band or the polaron band only from the optical absorption. The three PA bands are observed in the title compound $[Pt(en)_2][PtBr_2(en)_2](SO_4)_2{\cdot}6H_2O$ (en=ethylenediamine),[1] and their excitation spectra and photoconductivity are reported.[2,3] These results suggest that the "*C*–band" of the three PA bands is assigned to the polaron absorption band. However, the origins of the PA bands are not comprehensively understood. In an analogous complex $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$, the

PA bands and their assignment are reported in some literatures.[4-8] The PA bands of the perchlorate Cl-bridged complex in visible-light region are assigned to the soliton bands by a pressure-induced effect of the PA bands[4,5] and the analysis of the photo-induced ESR results.[9,10] It is important to investigate the optical absorption under high pressure in order to understand comprehensively the midgap PA bands. In addition, a phase transition of the sulfate Br-bridged complex can be expected from analogy with a pressure-induced phase transition of the perchlorate Cl-bridged complex.[11] Consequently, we have measured the absorption and resonance Raman spectra in single crystals of the sulfate Br-bridged complex in order to study the mixed-valence state, the midgap state and the pressure-induced phase transition under various hydrostatic pressures up to 3.7 GPa at room temperature.

EXPERIMENTAL

$[Pt(en)_2][PtBr_2(en)_2](SO_4)_2 \cdot 6H_2O$ was synthesized by a method described in a previous paper.[12] Single crystals were obtained by recrystallization from an aqueous solution on slow evaporation. The absorption spectra were measured at room temperature by using a multichannel spectrometer system with an Olympus BH20 microscope. A tungsten halogen lamp was used as the light source. Light of wavelength longer than 500 nm was obtained with a glass filter. Light transmitted through the crystal was dispersed with a monochromator Ritsu MC-30DG, and then detected by a CCD camera, Photometrics CH250. The Raman spectra were measured at room temperature by using a Spex Model 1877A triple stage spectrometer with a PAR Model 1254 SIT multichannel detector. The 5145 Å line of an Ar^+-ion laser was employed as the light source. The scattered light was observed in the nearly back-scattering configuration. The hydrostatic pressure was generated by using the clamp-type diamond-anvil cell. Inconel was used as the gasket, and Sumitomo 3M Flourinert FC40 was used as the pressure-transmitting medium for hydrostatic environment inside the pressure cell. Pressure was calibrated by measuring the wavelength shift of the R_1 luminescence line of the ruby crystal irradiated by an Ar^+-ion laser. In the measurement of the absorption, the sample was placed on a 10-μm-thick bare sheet of a Polaroid linear polarizer in the pressure cell. The installation of the polarizer into the pressure cell is requisite to avoid the depolarization due to strain in the diamonds. All the measurements of the absorption were performed with the polarization parallel to the Pt–Br chain axis because midgap and IVCT absorption bands are observable only for this polarization. In the measurement of Raman spectra, the polarization of the incident radiation was parallel to the Pt–Br chain axis, because the Pt–Br symmetric stretching vibration mode is intensely observed for this polarization.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of $[Pt(en)_2][PtBr_2(en)_2](SO_4)_2{\cdot}6H_2O$ for light polarized parallel to the Pt–Br chain axis at various pressures up to 3.1 GPa and at room temperature. The absorption feature is the edge of the absorption band assigned to the intervalence charge-transfer (IVCT) transition from "Pt^{II}" to "Pt^{IV}". The "Pt^{II}" and "Pt^{IV}" electronic states in the mixed-valence Pt complexes are rather closer in valence to the Pt^{III} state than the Pt^{II} and Pt^{IV} states in their constituent complexes, respectively, because of the intervalence charge-transfer interaction through the bridging bromide. The absorption edge monotonously shifts toward lower energies with increasing pressure up to 2 GPa. The shift of the absorption edge is reversible on releasing pressure from 2 GPa. Similar red shifts of the absorption edge with increasing pressure have been reported in $[Pt(C_2H_5NH_2)_4][PtCl_2(C_2H_5NH_2)_4]Cl_4{\cdot}4H_2O$[13,14] and $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$.[4] In the latter complex, an enhancement of the midgap absorption band has been observed with increasing pressure up to 2.1 GPa.[4] In the sulfate Br-bridged complex, however, no enhancement of the optical absorption in the region of the midgap absorption bands (*A*–, *B*– and *C*–bands) is observed; those peak energies are 1.6 eV, 1.8 eV and 2.1 eV, respectively. This result shows that the midgap state is not generated by applying pressure at room temperature.

A new absorption band appears around 1.2–1.5 eV above 2.5 GPa. Then, at 3.5 GPa, the optical density of the absorption spectrum grow above 2.3 in the spectral region 1.24–2.48 eV. The new absorption band has a hysteresis with pressure. The absorption does not change with decreasing pressure from 3.5 GPa up to 1.9 GPa. Namely, the absorption at 1.9 GPa on the decrease process of the pressure is different from that of the increase. In the crystals pressed once up to 3.5 GPa, the optical

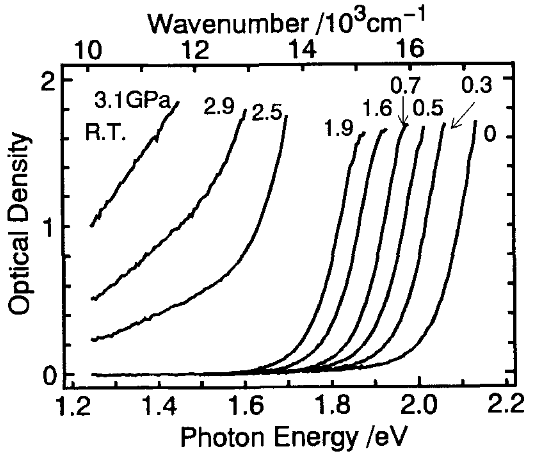

FIGURE 1 The absorption spectra of $[Pt(en)_2][PtBr_2(en)_2](SO_4)_2\cdot 6H_2O$ for the irradiated light polarized parallel to the Pt–Br chain axis at various pressures up to 3.1 GPa and at room temperature.

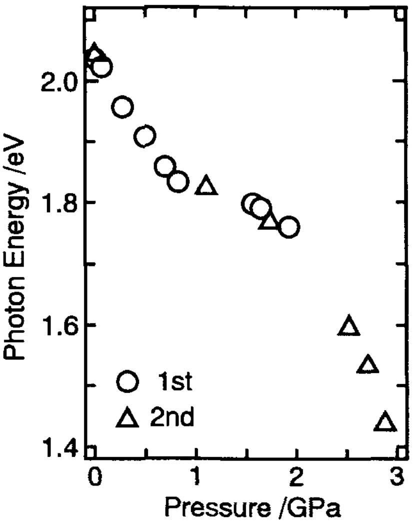

FIGURE 2 Pressure dependence of IVCT absorption edge.

absorption remaine below the absorption edge under atmospheric pressure. It suggests that a phase transition occurs in the crystals above 2.5 GPa. Moreover, the coefficient of the shift of the absorption edge with pressure in 1–2 GPa is smaller than those below 1 GPa and above 2 GPa as shown in Figure 2. The behavior in 1–2 GPa may be a symptom of a phase transition.

In the resonance Raman spectra, we observe the feature at about 185 cm^{-1} which is assigned to the Pt–Br symmetric stretching vibration mode, and its first overtone. The frequency of the fundamental mode decreases monotonously with increasing pressure up to about 3 GPa, but then increases with increasing pressure from 3 to 3.7 GPa, as shown in Figure 3. Figure 4 shows the dependence of the frequency of the fundamental Pt–Br stretching mode on pressure. The Raman peaks of the Pt–Br stretching mode are restored to their atmospheric pressure values upon completely releasing pressure from 3.7 GPa. In addition, a new Raman peak appears around 215 cm^{-1} if pressure exceeds 1.6 GPa. The new Raman peak is not observed under

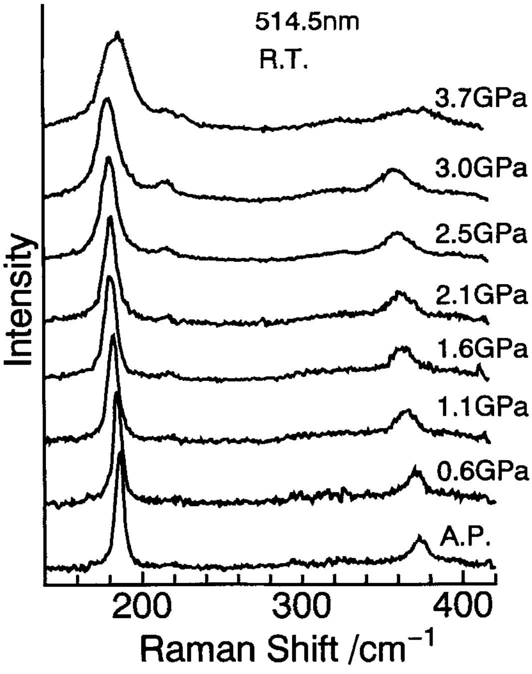

FIGURE 3 Resonance Raman spectra at various pressures at room temperature.

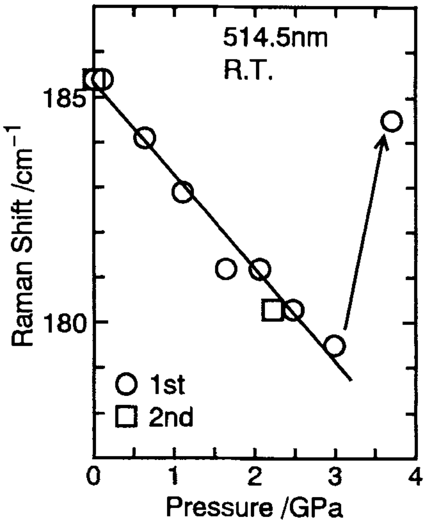

FIGURE 4 Pressure dependence of Raman shift.

atmospheric pressure released from 3.7 GPa, and exhibits no hysteresis with pressure, which is different from the new absorption band around 1.2–1.5 eV.

The red shifts of both the IVCT absorption edge and the Pt–Br stretching mode Raman peak with increasing pressure show that the energy gap in the mixed-valence "Pt^{II}" and "Pt^{IV}" state decreases, and that the bond energy between the platinum atom and the bromine atom decreases. The decrease of the Pt–Br bond energy corresponds to the approach of the bridging bromide to the midpoint between the neighboring platinum atoms in the chain. Namely, the results show the mixed-valence "Pt^{II}" and "Pt^{IV}" state approaches the single-valence Pt^{III} state with increasing pressure. On the other hand, the pressure-induced bands of the optical absorption and of the Raman spectrum suggest that a new phase coexists at pressures above 1.6 or 2.5 GPa. It is inferred from the following reason that the phase transition is a change of the Pt–Br chain from bent to straight with increasing pressure; the intervalence charge–transfer interaction between the platinum atoms through the bridging bromide ions in the chain increases due to the approach of the neighboring platinum atoms in the chain to each other by applying pressure. Namely, we consider that the increase of the intervalence charge–transfer interaction causes the straight Pt–Br chain and thus the new phase appears.

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