Bull. Chem. Soc. Jpn., 64, 1607—1612 (1991)

Insulator-to-Metal-to-Semiconductor Transitions of One-Dimensional Bis(1,2-dione dioximato)Pt(II) Complexes at High Pressures

Ichimin Shirotani,* Akira Kawamura, Kazunaga Suzuki, Wataru Utsumi,†
and Takehiko Yagi†
Muroran Institute of Technology, 27-1, Mizumoto, Muroran 050
† The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106
(Received December 12, 1990)

The electrical resistivities and absorption spectra of one-dimensional bis(1,2-dione dioximato)Pt(II) have been studied at high pressures. The resistivities of needle crystals of $Pt(dmg)_2$ and $Pt(bqd)_2$ were measured in detail under a quasi-hydrostatic pressure of up to 7 GPa. $Pt(dmg)_2$ is an insulator with a resistivity of 10^{15} Ω cm, and $Pt(bqd)_2$ is a semiconductor with 10^3 Ω cm at atmospheric pressure. A pressure-induced insulator (semiconductor)-to-metal transition was observed for both complexes. This transition arises from a crossing of the $5d_{z^2}$ valence and $6p_z$ conduction bands. When the pressure was further increasued, a metal-to-semiconductor transition took place at around the pressure that showed a resistivity minimum. A new pressure-induced absorption band was found in the visible region for the Pt complexes. The new band did not shift with pressure; the intensity of the band, however, increased with pressure over a narrow pressure region. The pressure-induced band may be due to intramolecular d–d transitions. The metal-to-semiconductor transition may arise from a change in the electronic states at high pressure, since no anomaly in the strucutre was observed.

Square planar d^8 metal complexes with various kinds of 1,2-dinoe dioximes (Fig. 1) crystallize in columnar structures. These columns are formed by complex molecules with metal–metal distances varying from 3.2 to 3.6 Å in the direction of the stacks.1) These poorly conducting one-dimensional complexes show an intersting behavior at high pressure. The electrical resistivity,2–5) electronic and infrared spectra,4–8) and crystal structure9) of the complexes have already been studied at high pressures. Their resistivities rapidly decrease and an absorption band ascribed to the d–p transition shifts remarkably to a longer wavelength with pressure. The electrical and optical properties of the complexes are very sensitive to the metal–metal distance in a linear chain.

Pressure-induced electrical and optical anomalies in bis(dimethylglyoximato)Pt(II), $Pt(dmg)_2$, were observed at around 6.5 GPa; the electrical resistivity drastically decreases, by a factor 10^{-16}, with increasing pressure up to the pressure that indicates a resistivity minimum.2,3) A new pressure-induced absorption band at around 540 nm was found above 6 GPa.4,5) Bis(1,2-benzoquinone dioximato)Pt(II), $Pt(bqd)_2$, has the shortest Pt–Pt distance (3.17 Å) in the known bis(1,2-dione dioximato)Pt(II)

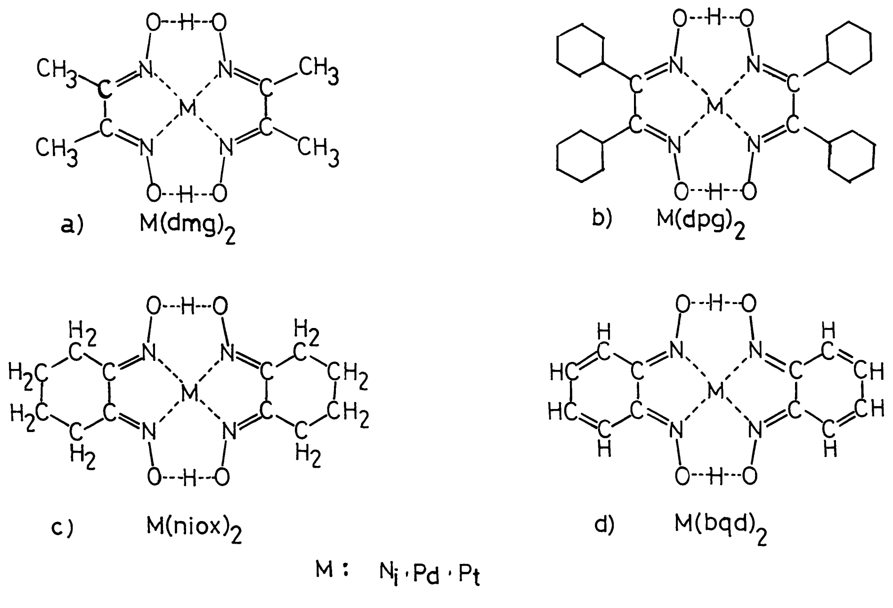

Fig. 1. Molecular structure of bis(1,2-dione dioximato)M(II) (M: Ni, Pd, Pt); a) bis(dimethylglyoximato)M(II), $M(dmg)_2$, b) bis(diphenylglyoximato)M(II), $M(dpg)_2$, c) bis(1,2-cyclohexanedione dioximato)M(II), $M(niox)_2$ (1,2-cyclohexanedione dioxime is usually called nioxime), d) bis(1,2-benzoquinone dioximato)M(II), $M(bqd)_2$.

compounds; it is a semiconductor with a thermal energy gap of 0.25 eV at atmospheric pressure.[10] The resistivity along the needle axis is about $10^3\ \Omega$ cm at room temperature. An absorption band polarized parallel to the linear chain, which is assigned to the electronic transition between $5d_{z^2}$ and $6p_z$, is located at around 1300 nm. The interesting properties are mainly interpreted in terms of a short Pt–Pt distance of 3.17 Å.

We recently reported preliminary results concerning insulator-to-metal-to-semiconductor transitions of $Pt(dmg)_2$ at high pressure; this complex behaves as an insulator(semiconductor) in the pressure range 0—4.5 GPa, as a metal around 5 GPa, and again as a semiconductor above 6 GPa.[5] Similar phenomena have also been observed for $Pt(bqd)_2$ at high presessures.

In this paper we present some findings concerning electrical and optical anomalies in the four platinum complexes shown in Fig. 1 and discuss the mechanism of the phase transitions at high pressure.

Experimental

Platinum complexes were prepared by mixing a hot alcohol solution of 1,2-dione dioximes and an aqueous solution of K_2PtCl_4. The products were purified by repeated recrystallization from *o*-dichlorobenzene or dimethylformamid. The needle crystals were grown from these solutions of the complexes. The compositions of all of the materials used were confirmed by elemental analysis.

Measurements of the electrical resistance were carried out up to 7 GPa in a cubic-anvil press; cemented tungusten carbide anvils had square faces of 6 mm edge length. Each sample was placed in the center hole of a pyrophyllite cube that had an 8 mm edge length. The sample assembly has already been reported in a previous paper.[12] The crystal was covered by an epoxy resin, which was used as a pressure-transmitting medium. The resistance was measured over a temperature range of 25 to 100 °C at various pressures under quasi-hydrostatic conditions.

A diamond-anvil pressure cell was used for the measurement of the absorption spectra at high pressures.[4] The optical system comprised a standard microscope and a monochrometer with an associated photodetection system. The pressure was determined from the pressure shift in the sharp R-line fluorescence spectrum of ruby.[13] Water was used as the pressure-transmitting medium.

Results and Discussion

$Pt(dmg)_2$ is a square planar complex in which each Pt^{2+} ion is surrounded by four nitrogen atoms of two dimethylglyoxime anions. The d orbitals of the Pt^{2+} ion are split by a crystal field of D_{4h} symmetry. The 8 electrons of the Pt^{2+} ion core fill the d_{z^2}, d_{xy}, d_{yz}, and d_{zx} states. The complex crystallizes in columnar structures. The columns are formed by square planar complex molecules with a relatively short Pt–Pt distance of 3.26 Å in a direction of the stacks. The overlap of the d_{z^2} orbitals can, thus, produced a band that is completely filled and separated from the next empty band formed by p_z orbitals by a large gap. The complex is an insulator with a resistivity of $10^{15}\ \Omega$ cm at atmospheric pressure.[14]

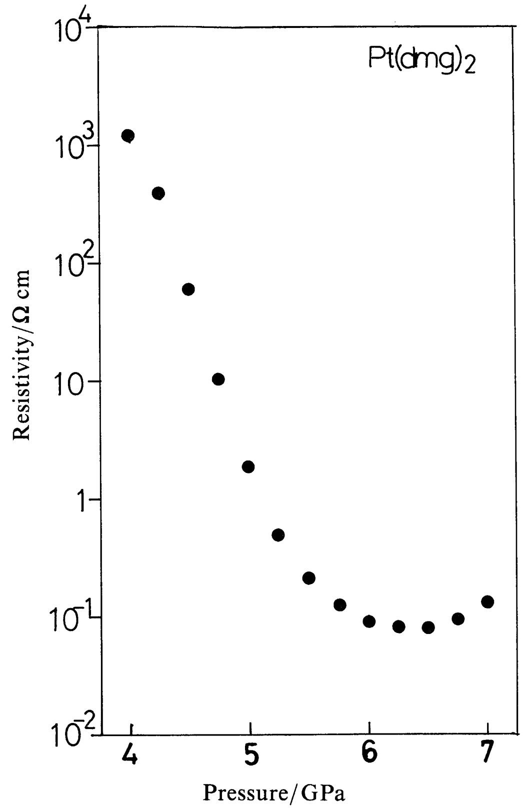

Fig. 2. Electrical resistivity of the single crystal of $Pt(dmg)_2$ at high pressure.

Figure 2 shows the electrical resistivity along the stacking axis of a single crystal of $Pt(dmg)_2$ at high pressures. The resistivity drastically decreases with pressure up to the pressure that shows the resistivity minimum. The lowest resistivity along the stacking axis of the single crystal is about $10^{-2}\ \Omega$ cm at room temperature and high pressure. Figure 3 shows the temperature dependence of the resistivity at various pressures. The resistivity linearly increases with increasing temperature at around 5 Gpa. A pressure-induced insulator-to-metal transition was observed. The thermal energy gap rapidly decreases with decreasing Pt–Pt distance, reaching zero at around 5 GPa.

The absorption spectrum of $Pt(dmg)_2$ comprises two bands at 320 and 660 nm in the visible region; the former band is ascribed to a metal-to-ligand charge-transfer transition (M–L transition); the latter band is assigned to the $5d_{z^2}$–$6p_z$ transition.[15] This latter band indicates a large red shift with pressure, at a rate of $-2700\ cm^{-1}/GPa$. Since the absorption edge is located at about $12.8\times10^3\ cm^{-1}$, the optical energy gap between the $5d_{z^2}$ and $6p_z$ bands becomes zero at around 5 GPa. Thus, the insulator-to-metal transition at around 5 GPa arises from a crossing of the $5d_{z^2}$ valence and the $6p_z$ conduction bands.

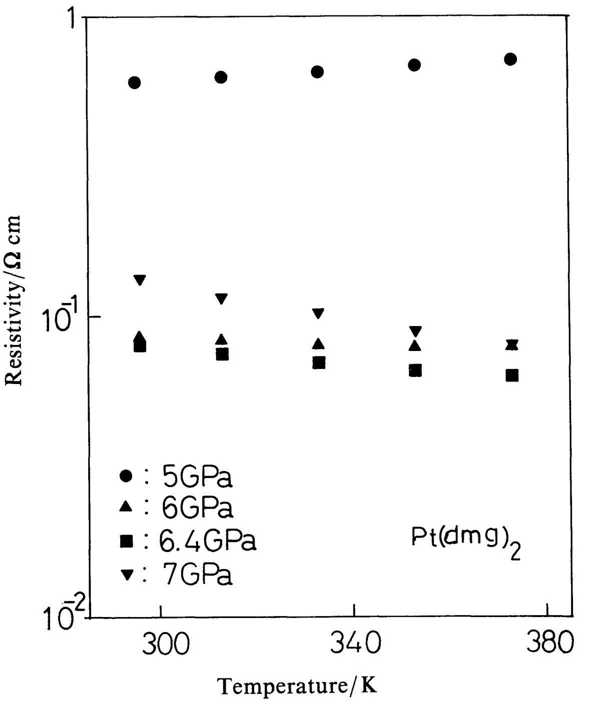

Fig. 3. Temperature dependence of the resistivity of $Pt(dmg)_2$ at high pressures.

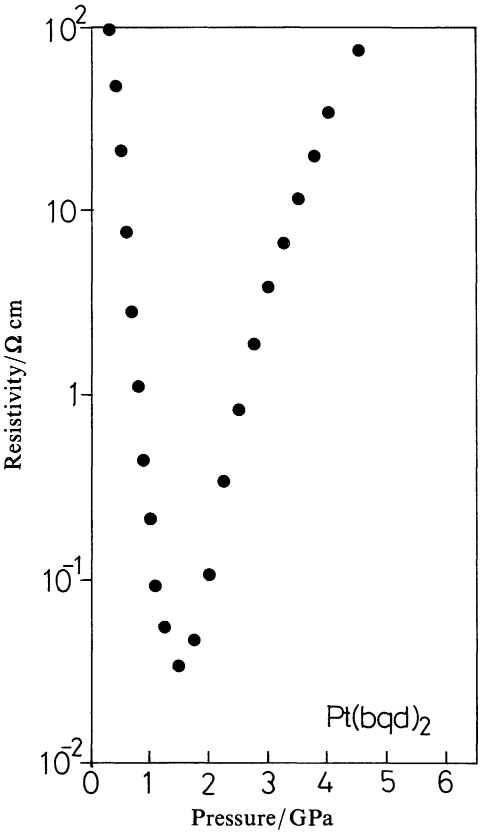

Fig. 4. Electrical resistivity of the needle crystal of $Pt(bqd)_2$ at high pressure.

The effect of pressure on the Pt–Pt distance has already been studied by powder X-ray diffraction.[4] The distance within a linear chain decreases from 3.26 Å at atmospheric pressure to 2.77 Å at 13 GPa. The Pt–Pt distance of metallic $Pt(dmg)_2$ is about 2.90 Å, slightly longer than that of a one-dimensional metal, such as $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KCP).

The temperature dependence of resistivity again changed at around 6 GPa; the resistivity slightly decreased with increasing temperature. Semiconductive-like behavior was again observed above 6 GPa. The one-dimensional metal was only stable within a narrow pressure region. This result seems to suggest a Peierls transition, due to the strong one-dimensional character in $Pt(dmg)_2$. Recently, an X-ray study of a single crystal of $Pt(dmg)_2$ was carried out up to 4 GPa.[9] The *a* and *b* lattice constants decrease monotonically with pressure. The Pt–Pt distance within the linear chains, $c/2$, decreases continuously from 3.26 Å at atmospheric pressure to 2.97 Å at 3.84 GPa. This agrees with the result concerning powder X-ray diffraction. The *b*-axis rapidly shrinks with pressure up to 1.5 GPa, but slowly decreases above this pressure. The intermolecular interaction of CH···O type grow stronger by a shrinking of the *b*-axis at high pressure. The intermolecular distance between O and C of the adjacent chains decreases from 3.28 Å at atmospheric pressure to 2.97 Å at 2.38 GPa. The intermolecular interaction between adjacent chains increases with pressure. The anomaly in the crystal structure along the *c*-axis, as anticipated for a Peierls distortion, was not found in the X-ray diffraction of the single crystal at around 7 GPa.[16]

A new pressure-induced absorption band appears at around 540 nm above 6 GPa.[3,4] The absorption intensity of the new band abruptly increases with increasing pressure over a narrow pressure range of 6 to 9 GPa. The absorption peak of the band does not shift with pressure at least up to 15 GPa. On the other hand, Tkacz and Drickamer have found that the intensity of the d–p band exhibits a sharp drop over the same pressure range.[7] The new band grows with a disappearance of the d–p transition. These results suggest that the metal-to-semiconductor transition at around 6 GPa is not due to a Peierls transition but, rather, to a change in the electronic states with pressure.

The resistivity of a needle crystal of $Pt(bqd)_2$ is about 10^3 Ω cm at room temperature.[10] The complex is a semiconductor with a thermal energy gap of 0.25 eV at atmospheric pressure. Figure 4 depicts the resistivity of a needle crystal at high pressure. The crystals were obtained by recrystallization from an *o*-dichlorobenzene solution. The resistivity rapidly decreases with pressure up to 1.7 GPa; above that pressure it abruptly increases with an increase in the pressure. The resistivity at the resistance minimum is about 10^{-2} Ω cm at room temperature and high pressure. Figure 5 shows the temperature dependence of the resistivity at various pressures. The resistivity rises with increasing temperature

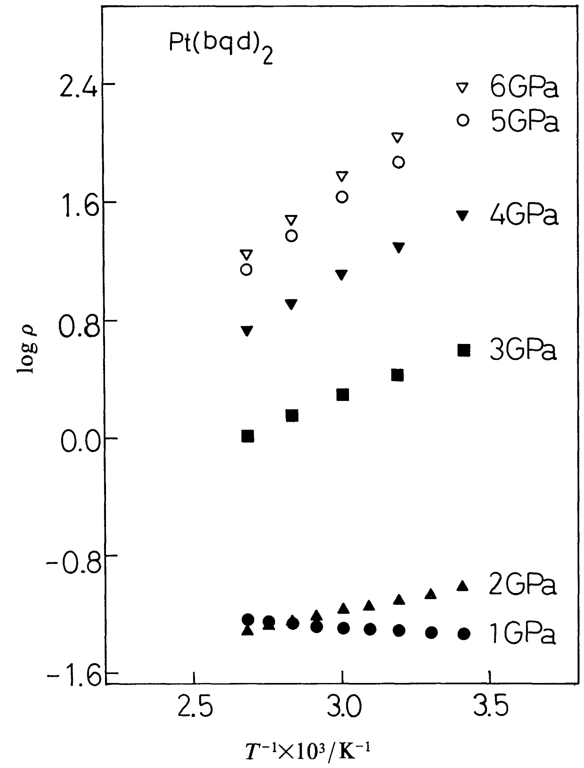

Fig. 5. Temperature dependence of the resistivity of Pt(bqd)$_2$ at high pressures.

at around 1 GPa. The thermal energy gap of 0.25 eV at atmospheric pressure became zero at around 1 GPa. A semiconductor-to-metal transition was found for Pt(bqd)$_2$.

An oriented film of Pt(bqd)$_2$ is prepared by evaporation onto a quartz or a glass substrate held at room temperature in a vacuum of 1.33×10^{-4} Pa (10^{-6} Torr, 1 Torr=133.322 Pa).[17] The absorption bands of the oriented film are located at around 360, 420, and 1300 nm. The latter band is assigned to the $5d_{z^2}$–$6p_z$ transtition. The pressure effect of the bands has not yet been studied. When the Pt–Pt distance of Pt(dmg)$_2$ skrinks from 3.26 Å to the Pt–Pt distance of Pt(bqd)$_2$ (3.17 Å), the peak of the d–p band shifts from 15200 to 13000 cm^{-1}. This value of Pt(dmg)$_2$ is much larger than the energy of the d–p band of Pt(bqd)$_2$, 7700 cm^{-1}. It is therefore expected that the d–p band of Pt(bqd)$_2$ has a very large red shift with pressure. The $6p_z$ conduction band must cross the $5d_{z^2}$ valence band at around 1 GPa.

The temperature dependence of the resistivity again changed at around 1.4 GPa; the resistivity of Pt(bqd)$_2$ decreased slightly with increasing temperature. The metal-to-insulator transition took place at around 1.4 GPa. The complex again behaved as a semiconductor above that pressure. The one-dimensional metal was stable within only a narrow pressure region. Figure 6 shows the absorption spectra of Pt(bqd)$_2$ at high pressures. A new pressure-induced absorption band appeared at around 660 nm above 1.3 GPa; the absorption intensity of the new band increased with pressure. The metal-to-semiconductor transition was found at around the pressure in which the optical anomaly was observed. Anomalous electronic and infrared spectra have been observed in a evaporated film of Pt(bqd)$_2$ on a NaCl substrate;[17] the 1300 nm band ascribed to the d–p transition disappears an asymmetric O···H–O bridge is formed, and the C=N stretching band splits into 1600 and 1610 cm^{-1}. The optical behavior of Pt(bqd)$_2$ is similar to that of Pt(dmg)$_2$ at high pressure.

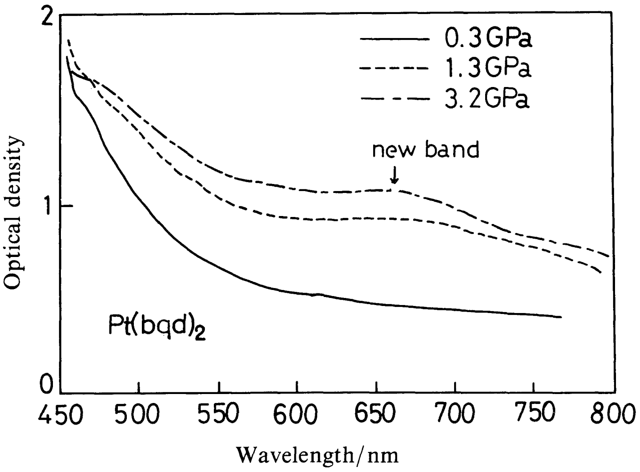

Fig. 6. Pressure effect of absorption spectra of Pt(bqd)$_2$.

The metal-to-semiconductor transition took place at around 6 GPa for Pt(dmg)$_2$, and 1.4 GPa for Pt(bqd)$_2$. The one-dimensional metal of both Pt complexes was stable over a very narrow pressure region. The pressure-induced absorption band and the resistivity minimum were observed near to the transition pressures. The absorption peaks of the new bands did not shift with pressure. An intramolecular d–d transition of metal complexes generally indicates a small blue shift with pressure.[6] The spin-allowed d–d transitions (d_{xy}–$d_{x^2-y^2}$, d_{z^2}–$d_{x^2-y^2}$, d_{yz} and d_{zx}–$d_{x^2-y^2}$) in square planar d^8 complexes can be observed, even though the absorption intensity is weak.[18] However, the transitions did not appear in the Pt complexes at atmospheric pressure. If vibronic modes of the complexes (especially the e_u mode) strongly couple to the d states with pressure, the intensity of the d–d transitions will increase at high pressure. The d–d transitions coupled by an e_u mode may borrow intensity from the M–L and d–p transitions. The absorption intensity of the d–p transition rapidly decreased over the narrow pressure region where the new band appeared. The pressure effect of the intensity of the M–L band has not been studied for Pt complexes. The a and b lattice constants (a=16.774 Å, b=10.579 Å) are so long that the $d_{x^2-y^2}$ orbitals between adjacent complex molecules in the ab plane hardly overlap. It is expected that the d–d bands hardly shift with pressure, since the $d_{x^2-y^2}$ orbital in the

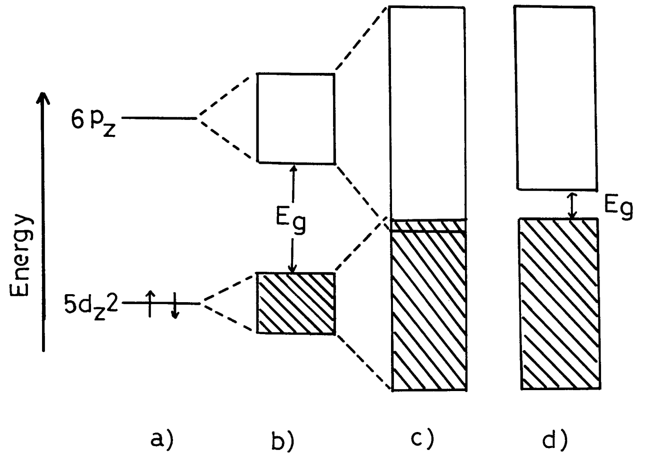

Fig. 7. Schematic energy diagram in $Pt(dmg)_2$ and $Pt(bqd)_2$ complexes; a) the energy separation between the filled $5d_{z^2}$ and the empty $6p_z$ orbitals of the complex molecules, b) the filled $5d_{z^2}$ valence and the empty $6p_z$ conduction bands are produced at atmospheric pressure, c) the $6p_z$ conduction band crosses the $5d_{z^2}$ valence band at high pressure. Pressure-induced insulator-to-metal transition takes place at room temperature, d) the energy gap between the $6p_z$ conduction and the $6p_{z^2}$ valence band is again observed at higher pressures. Pressure-induced metal-to-semiconductor transition takes place at room temperature.

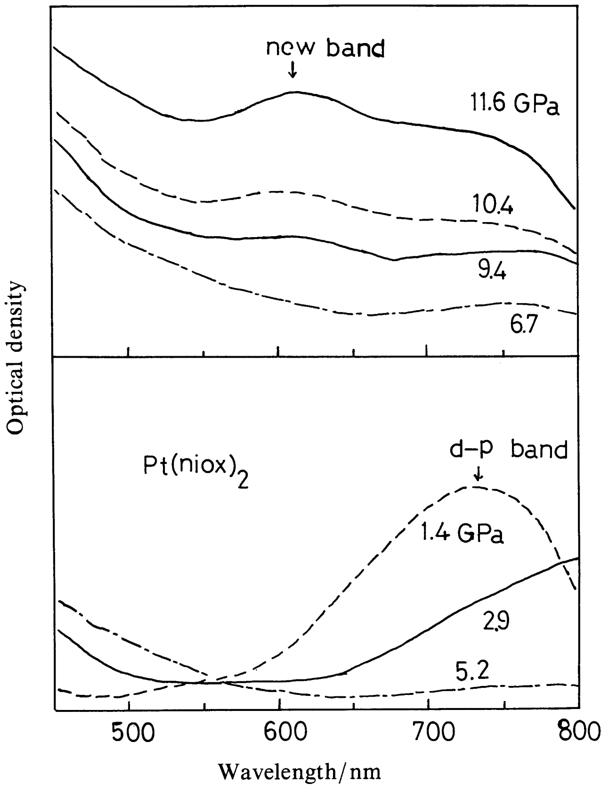

Fig. 8. Pressure effect of absorption spectra of $Pt(niox)_2$.

Pt complexes is not sensitive to pressure. We thus suggest that the new band of the Pt complexes is due to an intramolecular d–d transition as the intensity of the new band becomes stronger with pressure and the absorption peak does not shift with pressure. Therefore, the metal-to-semiconductor transition mainly arises from a change in the electronic states at high pressure.

We have found a pressure-induced insulator (semiconductor)-to-metal-to-semiconductor transitions for $Pt(dmg)_2$ and $Pt(bqd)_2$ over a narrow pressure region. A schematic energy diagram of the Pt complexes is given in Fig. 7.

A thin film of bis(1,2-cyclohexanedione dioximato)Pt(II), $Pt(niox)_2$, was prepared by evaporation in a high vacuum. The absorption spectrum of the thin film is similar to that of $Pt(dmg)_2$. The absorption bands of $Pt(niox)_2$ are located at 320 and 670 nm at atmospheric pressure; the former band is ascribed to the M–L transition, and the latter band is assigned to the d–p transition. Figure 8 exhibits the absorption spectra of $Pt(niox)_2$ at high pressures. The d–p band shifted remarkably toward longer wavelengths; the intensity of the band decreased with pressure. A new pressure-induced band at around 625 nm was observed above 9.5 GPa; the absorption intensity of the band increased with increasing pressure. The resistance of polycrystals of $Pt(niox)_2$ decreases rapidly with pressure, reaching a resistance minimum at 9.4 GPa.3) The lowest resistivity of the powder sample is about 2 Ω cm at high pressure. A pressure-induced band of $Pt(niox)_2$ was observed around the pressure showing the resistivity minimum. This behavior is smimilar to that of $Pt(dmg)_2$ and $Pt(bqd)_2$. A single crystal of $Pt(niox)_2$ has not yet been prepared. If the resistivity of the single crystal is measured in detail at high pressure, the phase transitions may be found.

The resistivity of bis(diphenylglyoximato)Pt(II), $Pt(dpg)_2$, decreased at least up to 22 GPa; no minimum was found. The lowest resistivity was 3×10^2 Ω cm at room temperature, much higher than that of the other Pt complexes. The band at 550 nm under atomospheric pressure is due to the $5d_{z^2}$–$6p_z$ transition, and the 394 nm band is assigned as the M–L transition. Both bands indicate large red shifts with pressure. No pressure-indued absorption band was found. No electrical or optical anomalies were found at high pressure.

References

1) E. Frasson, C. Panattoni, and R. Zannetti, *Acta Crystallogr.*, **12**, 1027 (1959); L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).

2) Y. Hara, I. Shirotani, and A. Onodera, *Solid State Commun.*, **19**, 171 (1976).

3) I. Shirotani, A. Onodera, and Y. Hara, *J. Solid State Chem.*, **40**, 180 (1981).

4) I. Shirotani and T. Suzuki, *Solid State Commun.*, **59**, 533 (1986).

5) I. Shirotani, M. Konno, and Y. Taniguchi, *Synth. Met.*, **29**, F123 (1989).

6) H. G. Drickarmer and J. C. Zhanar, *Adv. Chem. Phys.*, **4**, 161 (1962).

7) M. Tkacz and H. G. Drickamer, *J. Chem. Phys.*, **85**, 1184 (1986).

8) Y. Hara and M. Nicol, *Bull. Chem. Soc. Jpn.*, **51**, 1982 (1978).

9) M. Konno, T. Okamoto, and I. Shirotani, *Acta Crystallogh., Sect. B*, **45**, 142 (1989).

10) M. M. Bélombé, *J. Solid State Chem.*, **22**, 151 (1977).

11) J. W. Brill, M. M. Bélombé, and M. Novotny, *J. Chem. Phys.*, **68**, 585 (1978).

12) I. Shirotani, A. Fukizawa, H. Kawamura, T. Yagi, and S. Akimoto, "Solid State Physics under High Pressure," ed by S. Minomura, KTK Scientific Publisher, Tokyo (1985), p. 207.

13) J. D. Barnett, S. Block, and G. J. Piermarini, *Rev. Sci. Instrum.*, **44**, 1 (1973).

14) L. Atkinson, P. Day, and R. J. P. Williams, *Nature*, **218**, 668 (1968).

15) Y. Ohashi, I. Hanazaki, and S. Nagakura, *Inorg. Chem.*, **9**, 2551 (1970).

16) N. Hamaya, private communication.

17) I. Shirotani, N. Minobe, Y. Ohotsuki, H. Yamochi, and G. Saito, *Chem. Phys. Lett.*, **147**, 231 (1988).

18) H. B. Gray, "Transition Metal Chemistry," ed by R. L. Garlin, Marcel Dekker (1996).