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Pressure-Induced Insulator-to-Metal-to-Insulator Transitions in One-Dimensional Bis(dimethylglyoximato)platinum(II), Pt(dmg)$_2$

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Electrical resistivities, absorption spectra, and X-ray diffraction of one-dimensional bis(dimethylglyoximato)platinum(II), Pt(dmg)$_2$, have been studied in detail at high pressures. The resistivity drastically decreases with increasing pressure and reaches the minimum at around 6.5 GPa and then slowly increases with increasing pressure above this pressure. The pressure-induced insulator-to-metal-to-insulator (IMI) transitions in the complex have been found at around 5 and 6.5 GPa, respectively. The absorption spectra in the 25000−3000 cm^{-1} region were measured with a diamond-anvil cell up to 10 GPa at room temperature. The absorption band based on the 5d$_{z2}$−6p$_z$ transition at around 660 nm shifts remarkably to longer wavelengths with a rate of the pressure shift of − 2300 cm^{-1}/GPa. The optical energy gap between 5d$_{z2}$ and 6p$_z$ bands becomes zero at around 5 GPa. The absorption spectra of Pt(dmg)$_2$ markedly change at around the pressures which show the IMI transitions. By use of synchrotron radiation, the powder X-ray diffraction of Pt(dmg)$_2$ has been studied up to 10 GPa at room temperature. The lattice constants monotonically decrease with increasing pressure. The Pt−Pt distance within the chain, half of the *c*-axis, decreases continuously up to 10 GPa. The intermolecular interaction between the adjacent molecules increases remarkably with decreasing the *a*- and *b*-axes. However, the crystal structure does not change up to 10 GPa. The pressure-induced IMI transitions and the resistivity minimum arise from the change of the electronic states of Pt(dmg)$_2$ at high pressures.

Introduction

The interesting electrical and optical properties of one-dimensional *d*^{8}-platinum(II) complexes with various kinds of dionedioxime ligands have been studied; these complexes particularly have attracted much attention at high pressures. The absorption bands of these complex shift rapidly to longer wavelengths with increasing pressure.[1] The absorption band of bis(diphenylglyoximato)platinum(II) especially shows the large shift at the rate of − 3000 cm^{-1}/GPa in the low-pressure region. Then, the color of the complex markedly changes at high pressures. This material can be used as an indicator of pressure.[2] A remarkable decrease in the electrical resistance at high pressure with the characteristic resistivity minimum for some platinum complexes has been found at room temperature.[3]

Bis(dimethylglyoximato)platinum(II), Pt(dmg)$_2$, is a *d*^{8}-square−planar complex with the molecular structure shown in Figure 1. This complex is a single molecule, and the platinum in Pt(dmg)$_2$ is not partially oxidized. The crystal structure of the complex is orthorhombic, space group *Ibam*, and is indicated in Figure 2. The complex crystallizes in linear chain columnar structures. The columns are formed by square−planar complex molecules with a Pt−Pt distance of 3.26 Å in the direction of the stack.[4−6] The complex is an insulator with an electrical resistivity of 10^{15} Ω·cm at ambient pressure.[7,8] 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 the metal-to-ligand charge-transfer transition, and the latter band is assigned to the 5d$_{z2}$−6p$_z$ transition.[9]

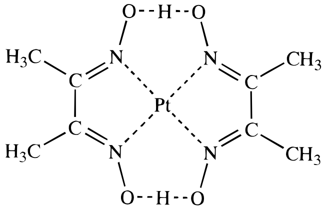

Figure 1. Molecular structure of Pt(dmg)$_2$.

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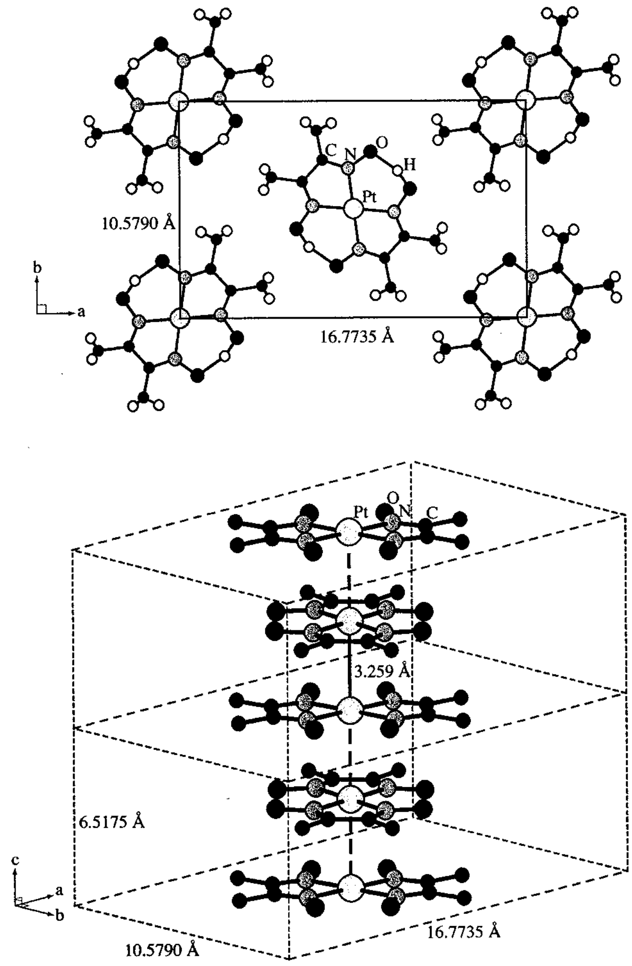

Figure 2. Crystal structure of Pt(dmg)$_2$.

Pt(dmg)$_2$ shows anomalous electrical and optical behavior at high pressures.[10,11] The electrical resistivity of the complex drastically decreases with increasing pressure up to 6.5 GPa. The temperature dependence of the resistivity increases with increasing temperature at around 5 GPa; the metallic behavior for the complex is observed at around this pressure. Above 6.5 GPa, the resistivity slowly increases with increasing pressure; the complex again shows the semiconducting behavior at around this pressure. The pressure-induced insulator-to-metal-to-insulator (IMI) transitions for Pt(dmg)$_2$ have been found at high pressures.[11] A new pressure-induced absorption band at around 540 nm is found at around 6 GPa.[10,11] The X-ray diffraction study of a single crystal of Pt(dmg)$_2$ has been carried out up to 4 GPa; the short contact between C and O atoms in the adjacent molecules is observed at around 2.4 GPa.[6]

The resistivity along the needle axis of a crystal for bis(1,2-benzoquinonedioximato)platinum(II), Pt(bqd)$_2$ is 3×10^2 Ω·cm at room temperature.[12] The absorption band assigned to the d−p transition is observed at around 8000 cm^{-1} for the complex.[13] This energy is much lower compared with that of the analogous d^8-complexes. The ionization energy obtained from the measurement of photoelectron spectra is 4.96 eV for the evaporated thin film of Pt(bqd)$_2$.[14] This value is comparable to that of tetrathiafulvalene (TTF), known as a good electron donor. The IMI transitions at high pressures have also been found for Pt(bqd)$_2$. [11,15] The nickel and palladium complexes do not show the IMI transitions at high pressures.[3,16]

We have studied in detail the electrical resistivity, the absorption spectra, and the powder X-ray diffraction with synchrotron radiation for Pt(dmg)$_2$ up to 10 GPa. In this paper, we discuss the origin of the pressure-induced IMI transitions and the resistivity minimum in the complex.

Experimental Section

Pt(dmg)$_2$ was prepared by mixing a hot water−ethanol solution containing stoichiometric amounts of K_2PtCl_4 and dimethylglyoxime. The products were purified by repeated recrystallization from *N*,*N*-dimethylformamide or dichlorobenzene.

The electrical resistivity was measured with a cubic anvil-type high-pressure apparatus up to 8 GPa.[11,17] The absorption spectra in the 400−3000 nm region were measured with a diamond-anvil cell up to 10 GPa at room temperature. The optical system comprised a standard microscope and a spectrophotometer with an associated photodetection system. A FT-IR (Nicolet MAGNA-IR760) was used for the measurement of the absorption spectra in the near-infrared region. A thin film of Pt(dmg)$_2$ was prepared by evaporation onto the surface of the diamond anvil in high vacuum.2) The thicknesses of the evaporated films are about 2000 Å. Fluorinert was used as the hydrostatic pressure fluid.

By use of synchrotron radiation, the powder X-ray diffraction of Pt(dmg)$_2$ was studied with the diamond-anvil cell and the imaging plate up to 10 GPa at room temperature.[15] The incident X-ray beam monochromatized to $\lambda = 0.6199$ Å was collimated to 40 nm in diameter. A 4:1 methanol−ethanol solution was used as the hydrostatic pressure fluid. The pressure in the diamond cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby.

Results

Figure 3a shows the electrical resistivity along the stacking axis of the single crystal of Pt(dmg)$_2$ at high pressures and at room temperature. The resistivity drastically decreases with pressure up to 6.5 GPa and then slowly increases with increasing pressure above this pressure. Figure 3b shows the temperature dependence of the resistivity ratio (ρ/ρ_0, where ρ_0 shows the resistivity at room temperature) at around 5 and 7 GPa. The resistivity slightly increases with increasing temperature at around 5 GPa. Pt(dmg)$_2$ shows the metallic behavior at around this pressure.[18] On the other hand, the resistivity slightly decreases with increasing temperature at 7 GPa. The complex again behaves as the insulator at this pressure. The IMI transitions are observed for Pt(dmg)$_2$ at high pressures.

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(18) Pt(dmg)$_2$ shows the metallic behavior at around 5 GPa. This may be semimetal. By our definition, “insulator” indicates an energy gap and “metal” indicates no energy gap.

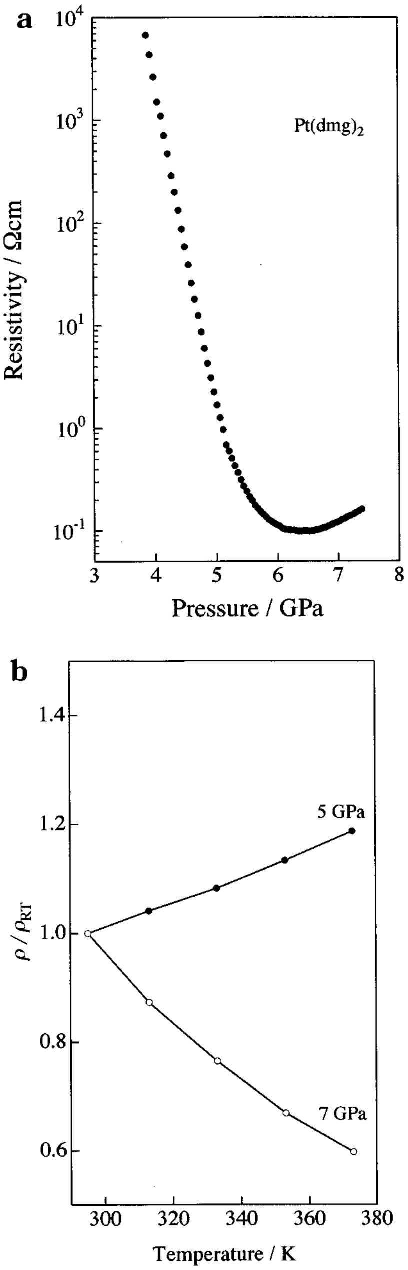

Figure 3. (a) Electrical resistivity along the *c*-axis of a single crystal of Pt(dmg)$_2$ at high pressures. (b) Temperature dependence of the resistivity ratio of Pt(dmg)$_2$ at around 5 and 7 GPa.

Figure 4a shows the absorption spectra of the thin film of Pt(dmg)$_2$ in the 25000−3000 cm^{-1} region at high pressures. Especially, we have studied in detail the absorption band in the near-infrared region at high pressure. The 5d$_{z^2}$−6p$_z$ transition band of Pt(dmg)$_2$ is observed at 15152 cm^{-1} (660 nm) at ambient pressure. The d−p band shifts remarkably to longer wavelengths with increasing pressure and appears in the near-infrared region above 1 GPa. A rate of the redshift of the band is −2300 cm^{-1}/GPa. Since the absorption edge is located at around 12 000 cm^{-1} at normal pressure, the optical energy gap between 5d$_{z^2}$ and 6p$_z$ bands becomes zero at around 5GPa. As mentioned above, this agrees with the result obtained from the temperature dependence of the electrical resistivity. The absorption spectra of Pt(dmg)$_2$ markedly change at around 5 GPa, which shows the metallic behavior. The pressure-induced absorption band appears at around 18500 cm^{-1}. This spectrum agrees with that of the powder sample reported in previous papers.[10,11] The intensity of the new band sharply increases with increasing pressure. If the polarized electronic spectra of the single crystal will be measured at high pressures, the origin of the pressure-induced band may be elucidated.

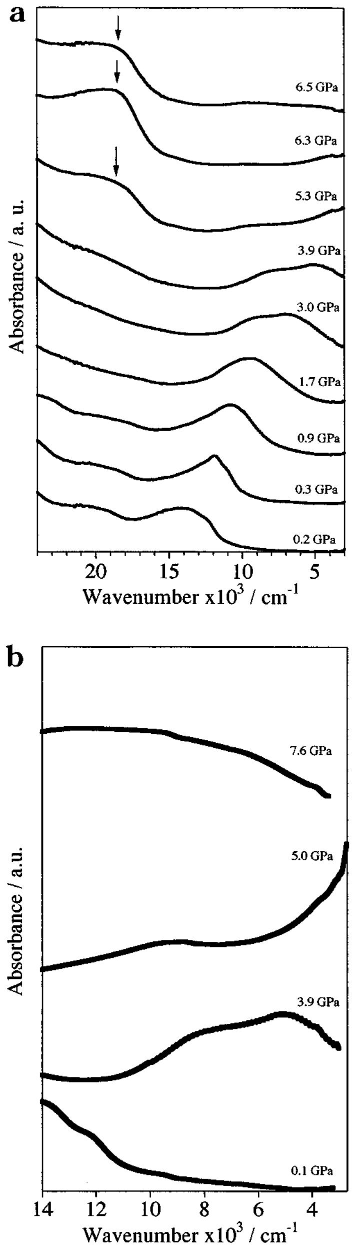

Figure 4. (a) Absorption spectra of Pt(dmg)$_2$ at high pressures. (b) Absorption spectra in the near-infrared region for Pt(dmg)$_2$ at high pressures.

Figure 4b shows absorption spectra of Pt(dmg)$_2$ in the near-infrared region at high pressures. The d−p band is observed at around 5000 cm^{-1} under 3.9 GPa, although the bandwidth broadens with pressure. The absorption peak based on the d−p transition disappears, and the absorption intensity in the 5000−3000 cm^{-1} region increases with decreasing wavenumber at around 5 GPa. On the other hand, Pt(dmg)$_2$ shows the semiconducting behavior at around 7.6 GPa. Then, the absorption intensity in the infrared region decreases with decreasing wavenumber. Therefore, this feature of

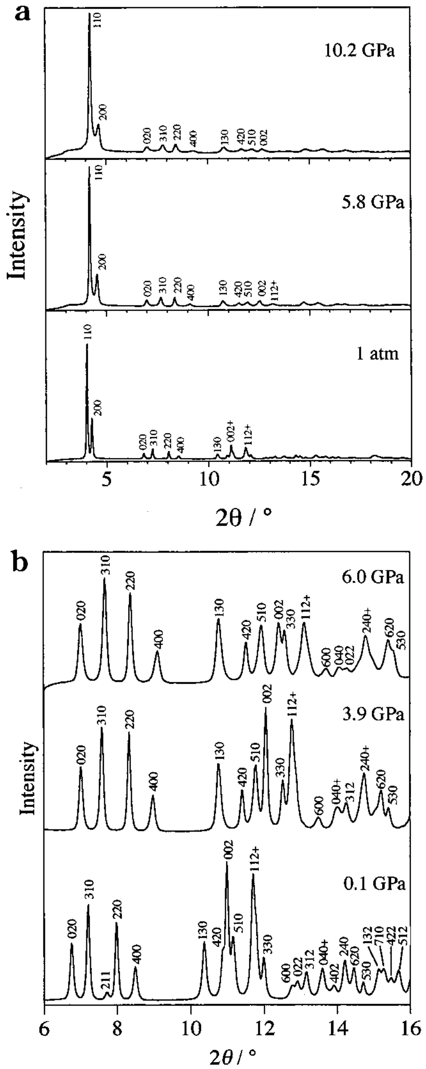

Figure 5. (a) Powder X-ray diffraction patterns of Pt(dmg)$_2$ at high pressures. (b) Powder X-ray diffraction patterns in high-angle region for Pt(dmg)$_2$ at high pressures.

the absorption spectra at high pressure is closely related to the IMI transitions.

An X-ray beam of synchrotron radiation is quite suitable for high-pressure experiments because of such excellent characteristics as brightness, a small divergence, and a constant energy. Especially, synchrotron radiation is available for X-ray study of organic compounds at high pressure. Using synchrotron radiation, we have studied the powder X-ray diffraction of Pt(dmg)$_2$ with the diamond anvil cell up to 10 GPa at room temperature. Figure 5a shows the X-ray diffraction patterns of Pt(dmg)$_2$ under various pressures. Two very strong diffraction lines, 110 and 200, of the complex are observed in the low-angle region. There are many diffraction lines in the high-angle region, but the intensity of these lines is much weaker than that of the 200 and 110 lines. All diffraction lines are assigned by the index of the orthorhombic structure (space group, *Ibam*).

Figure 5b shows the diffraction patterns in the high-angle region at high pressures. As the intensity of the diffraction lines is very weak, the measurement of the patterns is exposed to synchrotron radiation for long time (about 1 h). Then, the strong 110 and 200 lines are cut. The diffraction lines shift to the high-angle region with increasing pressure. Each line shows the different pressure shift. The *d* value of the 002 line agrees with the Pt−Pt distance in the linear chain of Pt(dmg)$_2$. This line is very sensitive to pressure. The powder X-ray diffraction patterns of the complex do not change basically up to 10 GPa, although the diffraction lines shift and broaden with increasing pressure. When pressure is reduced from 10 GPa to the ambient pressure, the diffraction pattern at normal pressure appears again at room temperature. This behavior is completely reversible.

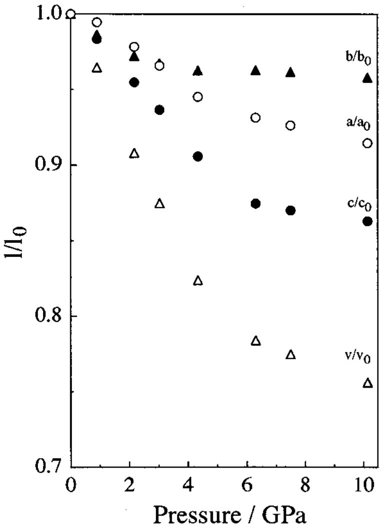

Figure 6. Ratio of lattice constants and volume of Pt(dmg)$_2$ at high pressures.

Figure 6 shows ratio of lattice constants (l/l_0, where l_0 = the value at ambient pressure) and cell volume versus pressure curves for Pt(dmg)$_2$. The lattice constants monotonically decrease with increasing pressure. The *b*-axis shows an initial larger decrease compared with that of the *a*-axis but is not sensitive to pressure above 2 GPa. The ratios of lattice constants at high pressures to those at atmospheric pressure show the largest shrinkage along the *c*-axis. The Pt−Pt separation within the chain, half of *c*, decreases continuously from 3.26 Å at ambient pressure to 2.9 Å at 5.0 GPa. This distance almost agrees with the Pt−Pt spacing of the one-dimensional metal, $K_2Pt(CN)_4Br_{0.3}3H_2O$. Furthermore, the Pt−Pt distance decreases with increasing pressure, being 2.8 Å at 10 GPa. This value is as large as the Pt−Pt distance in platinum metal.

As mentioned above, the one-dimensional metal in Pt(dmg)$_2$ is only stable between 5 and 6.5 GPa. This result may suggest a Peierls transition based on the one-dimensional character. An X-ray study of a single crystal of Pt(dmg)$_2$ has been carried out up to 7 GPa; the structural anomaly is not observed at room temperature.[11] On the other hand, the powder X-ray diffraction of Pt(bqd)$_2$ with synchrotron radiation has been studied at high pressures; the new diffraction lines appears between 200 and 110 lines in the orthorhombic structure at around 3.8 GPa.[15] This is due to the structural phase transition. However, the pressure of this transition is much higher than that of the IMI transitions.[11,15] Thus, we suggest that the IMI transitions for both Pt complexes are not due to the structural anomaly, but the change of the electronic states at high pressures.

Discussion

The Pt(dmg)$_2$ molecule is a d^8-square–planar complex; each Pt^{2+} ion is surrounded by four nitrogen atoms of two dimethylglyoxime anions. The 5d orbitals of a Pt^{2+} ion are split into four energy levels (d$_{xy}$, d$_{z2}$, d$_{yz}$, and d$_{zx}$, d$_{x2-y2}$) by a crystal field of D_{4h} symmetry, where d$_{yz}$ and d$_{zx}$ are double degeneracy. The eight d electrons of the Pt^{2+} ion core fill the d$_{z2}$, d$_{yz}$, d$_{zx}$, and d$_{x2-y2}$ states.

The complex crystallizes in columnar structures. The columns are formed by square–planar complex molecules with the relatively short Pt–Pt distance of 3.26 Å in the direction of the stacks. The overlap of the 5d$_{z2}$ orbitals can, thus, be produced a valence band that is completely filled by electrons. The conduction band is composed of 6p$_z$ orbitals. Both bands are separated by large energy gap at normal pressure.

As mentioned above, the resistivity of Pt(dmg)$_2$ drastically decreases with pressure up to the pressure that shows the resistivity minimum. The energy gap rapidly decreases with decreasing Pt–Pt distance, reaching zero at around 5 GPa. Then, the 6p$_z$ conduction band crosses the 5d$_{z2}$ valence band at around 5 GPa. The absorption peak based on the 5d$_{z2}$–6p$_z$ transition vanishes at around 5 GPa.

Above 6.5 GPa, the resistivity slowly increases with increasing pressure. Pt(dmg)$_2$ behaves as the insulator again at around 6.5 GPa. As shown in Figure 4a,b, the structural anomaly is not observed at high pressures. Thus, the IMI transitions arise from the change of the electronic states.

The Pt–Pt distance monotonically decreases with increasing pressure even above 6.5 GPa. Since the width of the 5d$_{z2}$ and 6p$_z$ bands must be increased with pressure, the metallic phase should be stabilized at higher pressures. However, Pt(dmg)$_2$ changes from the metal to the insulator at 6.5 GPa. This result suggests that the electrical behavior of Pt(dmg)$_2$ cannot be explained by the model of two bands (5d$_{z2}$ and 6p$_z$) above the pressure that shows the resistivity minimum.

Bella et al. have been studied the photoelectron spectra of the molecules of glyoximato (gly) and dimethylglyoximato (dmg) complexes of Pd(II) and Pt(II). The spectra of these complex are assigned by ab initio LCAO-MO SCF calculations.[19] Figure 7 shows the schematic energy diagram of the Pt(dmg)$_2$ molecule obtained by them. The top of the valence band consists of the 9a$_g$ molecular orbital (d$_{z2}$ character, metal-based molecular orbital). There is the 3b$_{3g}$ orbital (d$_{yz}$ and π_4 character, ligand-based molecular orbital) below the energy level of the 9a$_g$ orbital.

The X-ray study of the Pt(dmg)$_2$ single crystal at high pressure indicates that the intermolecular distance between O and C atoms of the adjacent chains decreases from 3.28 Å at normal pressure to 2.97 Å at 2.4 GPa.[6] This distance is much shorter than the sum (3.40 Å) of the van der Waals radii (O = 1.40 Å, C = 2.0 Å). The marked change in the C=N stretching mode for Pt(dmg)$_2$ appears at 2–3 GPa.[1,20] As shown in Figure 4b, the *a*- and *b*-axes shrink with pressure up to 10 GPa. The intermolecular interactions in the *ab*-plane grow stronger by the shrinking of the *a*- and *b*-axes at higher pressures. The electron cloud of the 9a$_g$(d$_{z2}$) orbital mainly spreads out in the direction of the metal chain, and in contrast, the 3b$_{3g}$ orbital is the ligand-based molecular orbital, expanding over the molecular plane. The 3b$_{3g}$ molecular orbital may be unstabilized with an increase of the intermolecular interaction between the adjacent molecules. Thus, we suggest that the top of the valence band changes from the 9a$_g$ to the 3b$_{3g}$ orbital at higher pressures. The 6p$_z$ conduction band and the new 3b$_{3g}$ valence band are separated with pressure above 6.5 GPa. Therefore, the resistivity minimum and the metal-to-insulator transition at around 6.5 GPa arise from the change of the electronic states.

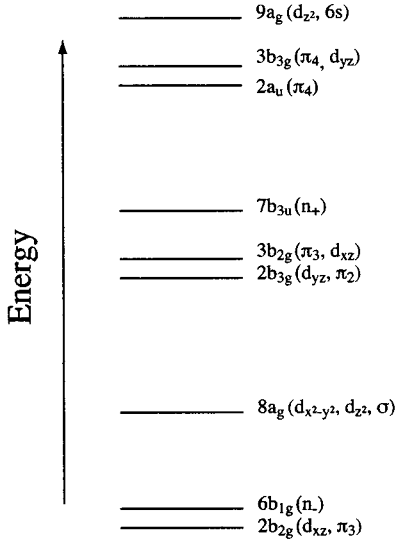

Figure 7. Schematic energy diagram in the valence band for a Pt(dmg)$_2$ molecule.

The highest lying occupied molecular orbitals (HOMO) of Pd(gly)$_2$ and Pd(dmg)$_2$ molecules consists of the 3b$_{3g}$ orbital (ligand-based molecular orbital) at normal pressure.[19] Ni(gly)$_2$ has similar electronic states.[21] The top of the valence band of the bis(1,2-benzoquinonedioximato)nickel(II), Ni(bqd)$_2$, complex consists of the ligand-based molecular orbitals.[22] The energy level of the 9a$_g$ orbital in Pd and Ni complexes is lower than that of the 3b$_{3g}$ orbital. The electronic states of both complexes are different than those of Pt complexes at atmospheric pressure. However, we suggest that the HOMO of Pt(dmg)$_2$ is displaced from the metal-based orbital to the ligand-based orbital at higher pressures.

The pressure-induced IMI transitions and the resistivity minimum have also been found for Pt(bqd)$_2$ at high pressures.[11,15] The structural, electrical, and optical properties of the complex have been studied in detail at high pressures. These results will be reported elsewhere.

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