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2000 J. Phys.: Condens. Matter 12 L483

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## LETTER TO THE EDITOR

**Metal to insulator transition of one-dimensional bis(1,2-benzoquinonedioximato)-platinum(II), Pt(bqd)<sub>2</sub>, at low temperatures and high pressures**Keiki Takeda<sup>†</sup>, Ichimin Shirotani<sup>†</sup>, Chihiro Sekine<sup>†</sup> and Kyuya Yakushi<sup>‡</sup><sup>†</sup>Muroran Institute of Technology, 27-1, Mizumoto, Muroran-shi 050-8585, Japan<sup>‡</sup>Institute for Molecular Science, Myodaiji, Okazaki-shi 444-8585, Japan

Received 13 April 2000, in final form 15 June 2000

**Abstract.** The electrical resistivity of the high quality single crystals of one-dimensional bis(1,2-benzoquinonedioximato)platinum(II), Pt(bqd)<sub>2</sub>, has been studied at low temperatures and high pressures under hydrostatic conditions. The resistivity along the *c*-axis abruptly decreases with increasing pressure up to 0.9 GPa at room temperature. Pt(bqd)<sub>2</sub> with an energy gap of about 0.3 eV at ambient pressure indicates the insulator-to-metal (IM) transition at around 0.8 GPa. The x-ray diffraction and the electronic spectrum of Pt(bqd)<sub>2</sub> have been studied at room temperature and high pressures. The mechanism of the IM transition of Pt(bqd)<sub>2</sub> is discussed. Below 235 K the resistivity of Pt(bqd)<sub>2</sub> increases with decreasing temperature at around 0.8 GPa. The metal-to-insulator (MI) transition for Pt(bqd)<sub>2</sub> is found at around 235 K under 0.8 GPa. This is the first example that the one-dimensional metal formed from single molecules shows the MI transition at low temperatures.

**1. Introduction**

One-dimensional bis(dimethylglyoximato)platinum(II), Pt(dmg)<sub>2</sub>, is an insulator with an electrical resistivity of  $10^{15}$  Ω cm at ambient pressure [1]. However, the compound shows anomalous electrical and optical properties at high pressures [2–5]. The electrical resistivity of the compound drastically decreases with increasing pressure up to 6.5 GPa. Metallic behaviour of Pt(dmg)<sub>2</sub> is observed at around 5 GPa. Above 6.5 GPa the resistivity slowly increases with increasing pressure; the complex again shows the semiconducting behaviour at around this pressure. The insulator-to-metal-to-insulator transitions for Pt(dmg)<sub>2</sub> have been found above room temperature at high pressures [4, 5].

Figure 1 shows the molecular structure of bis(1,2-benzoquinonedioximato)-platinum(II), Pt(bqd)<sub>2</sub>. The valence of the platinum is +2, not partially oxidized. The compound is a single molecule. Pt(bqd)<sub>2</sub> crystallizes in a one-dimensional columnar structure and has the shortest Pt–Pt distance (3.17 Å) of any known d<sup>8</sup>-bis(1,2-dionedioximato)platinum(II) complex [6]. The resistivities of Pt(bqd)<sub>2</sub> are  $3 \times 10^2$  Ω cm along the needle axis of the single crystal [7] and  $2 \times 10^3$  Ω cm for the oriented film [8] at room temperature. The compound is a semiconductor with a thermal energy gap of 0.25–0.35 eV. The resistivity of Pt(bqd)<sub>2</sub> rapidly decreases with increasing pressure up to 1.7 GPa and then increases with increasing pressure under quasi-hydrostatic conditions [4]. Electronic and photoelectron spectra of Pt(bqd)<sub>2</sub> have been studied at ambient pressure [9, 10].

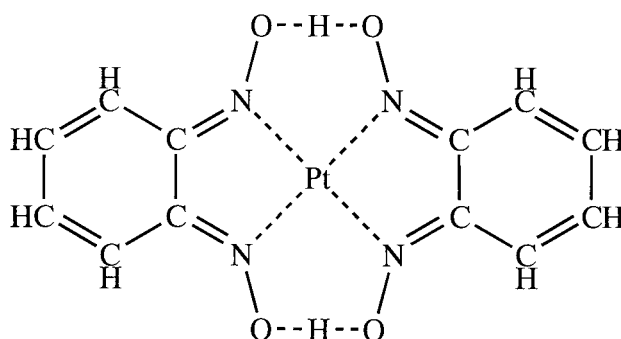


Figure 1. Molecular structure of Pt(bqd)<sub>2</sub>.

We have prepared high quality single crystals of Pt(bqd)<sub>2</sub> using the diffusion method, and have measured the resistivity of the single crystals at low temperatures and high pressures. Pt(bqd)<sub>2</sub> shows metallic behaviour at around 0.8 GPa. Further, the metal-to-insulator (MI) transition for this compound is found at around 235 K under 0.8 GPa. In this report the MI transition of Pt(bqd)<sub>2</sub> is discussed.

## 2. Experiment

*o*-Benzoquinonedioxime (*o*-bqd) was synthesized from commercially available *o*-nitrosoaniline, which was oxidized with basic NaOCl to give *o*-nitrosobenzen. Then, it was reduced with basic NH<sub>2</sub>OH·HCl in ethanol to yield *o*-bqd. Pt(bqd)<sub>2</sub> was prepared by mixing a hot water–ethanol solution containing stoichiometric amounts of K<sub>2</sub>PtCl<sub>4</sub> and *o*-bqd [7, 10]. The single crystals of Pt(bqd)<sub>2</sub> were slowly grown by the diffusion of *o*-bqd in the acetone solution and K<sub>2</sub>PtCl<sub>4</sub> in the aqueous solution. We obtained good needle crystals with a size of 4 × 0.2 × 0.025 mm. The crystals appear black and opaque under reflected light.

The high-pressure apparatus to measure the resistivity is basically similar to the device designed by Oumi *et al* with some improvement [11]. The load is always kept constant by controlling the oil pressure of the hydraulic press. Thus, there is no pressure change during either the cooling or heating processes. A piston cylinder-type high-pressure cell was used in this experiment. A mixture of Fluorinert (No FC70 and 77) was used as the pressure-transmitting fluid. The electrical resistivity at low temperature and high pressure was measured by means of a four-probe technique under hydrostatic conditions from room temperature down to 77 K.

Using synchrotron radiation the powder x-ray diffraction of Pt(bqd)<sub>2</sub> was studied with a diamond-anvil cell and an imaging plate, up to 3 GPa at room temperature [12]. The incident x-ray beam monochromatized to  $\lambda = 0.6199 \text{ \AA}$  was collimated to 40 nm in diameter. The absorption spectra in the 500–3000 nm region were measured using a diamond-anvil cell 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 [5]. The pressure in the diamond-cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby.

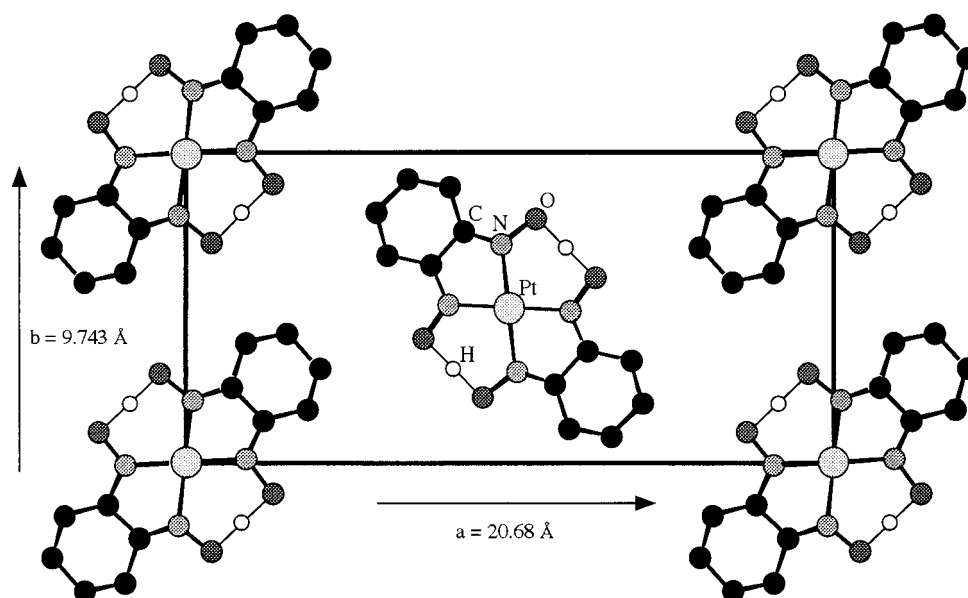


Figure 2. Crystal structure of Pt(bqd)<sub>2</sub>.

### 3. Results and discussion

Figure 2 shows the crystal structure of Pt(bqd)<sub>2</sub>. The structure is orthorhombic, space group *Ibam*; the lattice constants are  $a = 20.68 \text{ \AA}$ ,  $b = 9.743 \text{ \AA}$ ,  $c = 6.346 \text{ \AA}$ ,  $V = 1279 \text{ \AA}^3$ ,  $Z = 4$  [6]. The lattice is built up of neutral, completely coplanar Pt(bqd)<sub>2</sub> molecules, which are aligned in finite chains with a Pt–Pt distance of  $3.17 \text{ \AA}$ . The powder x-ray diffraction of Pt(bqd)<sub>2</sub> has been studied with synchrotron radiation at high pressure and at room temperature [12]. Figure 3 shows the ratio of lattice constants ( $l/l_0$ ) for Pt(bqd)<sub>2</sub> at high pressures. The lattice constants decrease with increasing pressure; the *c*-axis is very sensitive to pressure.

Figure 4 shows the pressure dependence of the electrical resistivity along the *c*-axis of the single crystal of Pt(bqd)<sub>2</sub> at room temperature under hydrostatic conditions. The resistivity decreases with increasing pressure and sharply drops at around 0.9 GPa. Figure 5 shows the resistivity versus temperature curve for the compound at around 0.8 GPa, below room temperature. The resistivity decreases with decreasing temperature from room temperature down to 235 K. The insulator-to-metal transition is observed at around 0.8 GPa. This transition pressure is much lower than that of Pt(dmgl)<sub>2</sub> [4, 5].

The resistivity of Pt(bqd)<sub>2</sub> increases with increasing pressure above 0.9 GPa. The semiconducting behaviour also is observed above 1 GPa. The insulator-to-metal-to-insulator transitions for Pt(bqd)<sub>2</sub> have been found in the low pressure region. This electrical behaviour of Pt(bqd)<sub>2</sub> is similar to that of Pt(dmgl)<sub>2</sub> at high pressure [4, 5].

The absorption band of Pt(bqd)<sub>2</sub> is located at around  $8000 \text{ cm}^{-1}$  (1 eV) at ambient pressure. This band is assigned to the  $5d_{z^2}$  to  $6p_z$  transition [9, 10]. The d–p band shifts to longer wavelength with increasing pressure and disappears at around the pressure indicating metallic behaviour. The feature of the absorption spectra at high pressures is closely related to the insulator-to-metal transition. The molecular and crystal structures of Pt(dmgl)<sub>2</sub> are similar to those of Pt(bqd)<sub>2</sub>. Pt(dmgl)<sub>2</sub> shows metallic behaviour at around 5 GPa. The absorption spectra

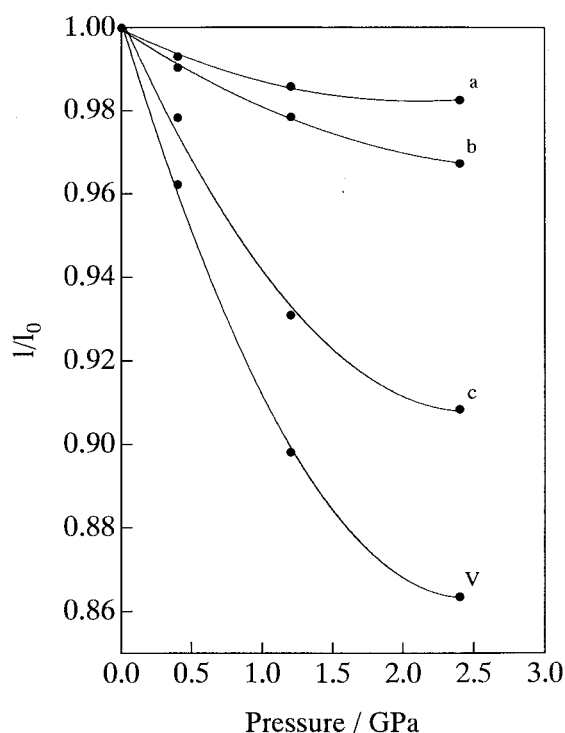


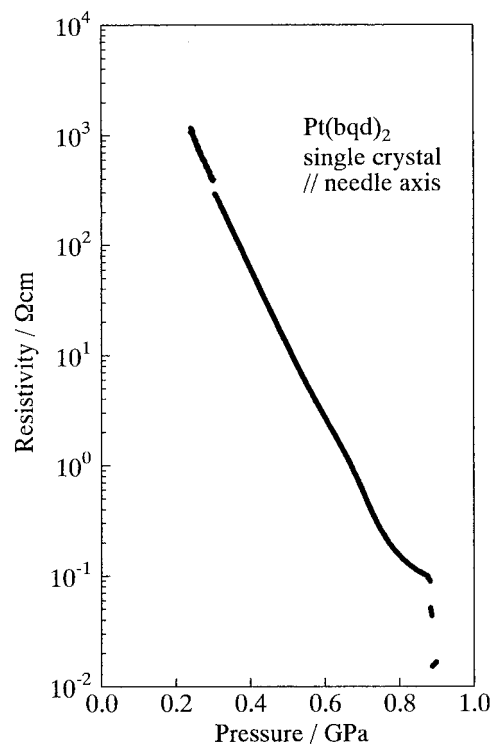
Figure 3. Ratio of lattice constants ( $l/l_0$ ) versus pressure curve for  $\text{Pt}(\text{bqd})_2$  at room temperature.

in the near infrared region for the compound abruptly change at around 5 GPa [5]. The optical behaviour of  $\text{Pt}(\text{dmg})_2$  at high pressures is similar to that of  $\text{Pt}(\text{bqd})_2$ . The electronic spectra of  $\text{Pt}(\text{bqd})_2$  will be reported in detail elsewhere.

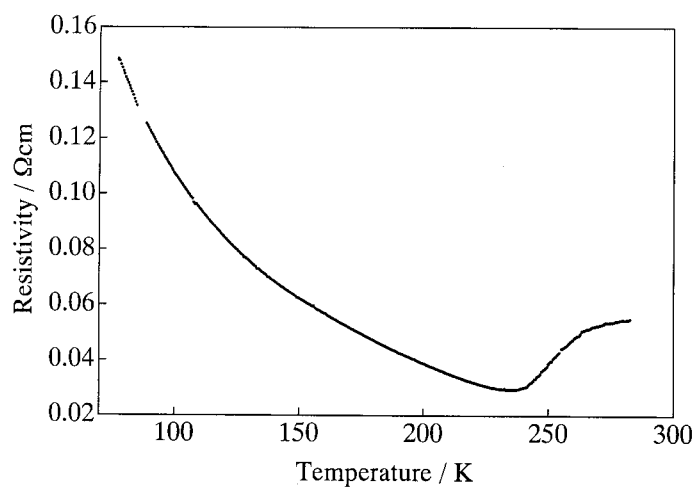
Below 235 K the resistivity increases with decreasing temperature at around 0.8 GPa. The metal-to-insulator transition of  $\text{Pt}(\text{bqd})_2$  is found at around 235 K under 0.8 GPa.

A  $\text{Pt}^{2+}$  ion in a  $\text{Pt}(\text{bqd})_2$  molecule is surrounded by four nitrogen atoms of two *o*-benzoquinonedioxime anions. The 5d orbitals of the  $\text{Pt}^{2+}$  ion are split into four energy levels ( $d_{xy}$ ,  $d_{z^2}$ ,  $d_{yz}$  and  $d_{zx}$ ,  $d_{x^2-y^2}$ ) by a ligand field of  $D_{4h}$  symmetry, where  $d_{yz}$  and  $d_{zx}$  are double degeneracy. The eight d electrons of the  $\text{Pt}^{2+}$  ion core fill the  $d_{z^2}$ ,  $d_{yz}$ ,  $d_{zx}$  and  $d_{x^2-y^2}$  states [13].  $\text{Pt}(\text{bqd})_2$  crystallizes in columnar structures with a one-dimensional character. Thus, the overlap of the  $5d_{z^2}$  orbitals can produce a valence band that is completely filled by d electrons. The conduction band is composed of  $6p_z$  orbitals. Both bands in  $\text{Pt}(\text{bqd})_2$  are separated by an energy gap of about 0.3 eV at ambient pressure. The energy gap rapidly decreases with decreasing Pt–Pt distance, reaching zero at around 0.8 GPa. Then, the  $6p_z$  conduction band crosses the  $5d_{z^2}$  valence band at this pressure. Thus,  $\text{Pt}(\text{bqd})_2$  indicates the insulator-to-metal transition above 235 K at around 0.8 GPa.

The Pt–Pt distance decreases from 3.17 Å at ambient pressure to 3.01 Å at 0.8 GPa. This value is longer than the Pt–Pt distance (= 2.86 Å) in one-dimensional metal  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$ . The d electrons are delocalized in the metal chain though the Pt–Pt distance in  $\text{Pt}(\text{bqd})_2$  is considerably long. A possible mechanism for this delocalization may be provided by the backbonding formalism [7]. The filled d orbitals (mainly,  $d_{yz}$  and  $d_{xz}$ ) of the central metal are hybridized with empty  $\pi^*$  orbitals of the coordinating ligand atoms.



**Figure 4.** Pressure dependence of the electrical resistivity along the  $c$ -axis of the single crystal of  $\text{Pt}(\text{bqd})_2$  at room temperature under hydrostatic conditions.



**Figure 5.** Resistivity versus temperature curve for  $\text{Pt}(\text{bqd})_2$  at around 0.8 GPa, and below room temperature.

The d electrons in the metal penetrate into the ligand. Thus, as the d electron density on the platinum metal is reduced to some extent, the electron repulsion becomes small.

When the temperature is reduced below 235 K, the MI transition for Pt(bqd)<sub>2</sub> is observed. The compound is a single molecule. This is the first example that the one-dimensional metal formed from single molecules shows the MI transition at low temperatures.

TTF–TCNQ is the donor–acceptor complex and is known to be a one-dimensional metal at room temperature. The MI transition for the molecular complex occurs at around 60 K [14]. A similar transition is also observed for the molecular complexes consisting of the TTF analogues. The MI transition of the molecular complexes arises from the Peierls distortion based on a strong one-dimensional character. Pt(bqd)<sub>2</sub> has this one-dimensional characteristic. The MI transition of Pt(bqd)<sub>2</sub> may be due to the Peierls transition.

Iodanil (C<sub>6</sub>I<sub>4</sub>O<sub>2</sub>) is an organic single molecule and is an insulator with a resistivity of 10<sup>12</sup> Ω cm at ambient pressure [15]. The resistivity rapidly decreases with increasing pressure. The insulator-to-metal transition of the compound occurs at around 30 GPa. However, the metallic iodanil does not show the MI transition at low temperatures, though it does show superconductivity at around 2 K [16]. The crystal structure of iodanil suggests the three-dimensional interactions [17]. Thus, the one-dimensional character in the crystal structure of Pt(bqd)<sub>2</sub> plays an important role for the MI transition at low temperatures.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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