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X-Ray Study with Synchrotron Radiation for the One-Dimensional Complex Bis(1,2-Benzoquinonedioximato)Platinum(II), $Pt(BQD)_2$, at High Pressures

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By use of synchrotron radiation, powder x-ray diffraction patterns of the one-dimensional complex bis(1,2-benzoquinonedioximato)platinum(II), $Pt(bqd)_2$, have been measured at high pressures. The pressure dependence of the lattice constants with an orthorhombic structure in this complex was studied at room temperature. The c-axis (twice the Pt–Pt distance) decreases monotonically with an increasing pressure of up to 5 GPa at room temperature. However, the a-axis increases abruptly at around 2 GPa; the b-axis decreases rapidly at around this pressure. We have found the anomalous pressure dependence of the lattice parameters above 2 GPa. Ratios of a- and b-axes, a/b for $Pt(bqd)_2$, are 2.123 at ambient pressure and 2.434 at 4.4 GPa. The crystal structure of $Pt(bqd)_2$ becomes more anisotropic at higher pressures. The anomalous structural behavior of $Pt(bqd)_2$ at high pressure is discussed.

Keywords: high pressure; one-dimensional Pt complex; structure; synchrotron radiation; x-ray diffraction

INTRODUCTION

The anomalous electrical and optical behavior of one-dimensional d^8-platinum(II) complexes with dionedioxime ligands has already been

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found at high pressures [1,2]. Absorption bands of these complexes shift rapidly to longer wavelengths with increasing pressure. The absorption band of bis(diphenylglyoximato)platinum(II), $Pt(dpg)_2$,

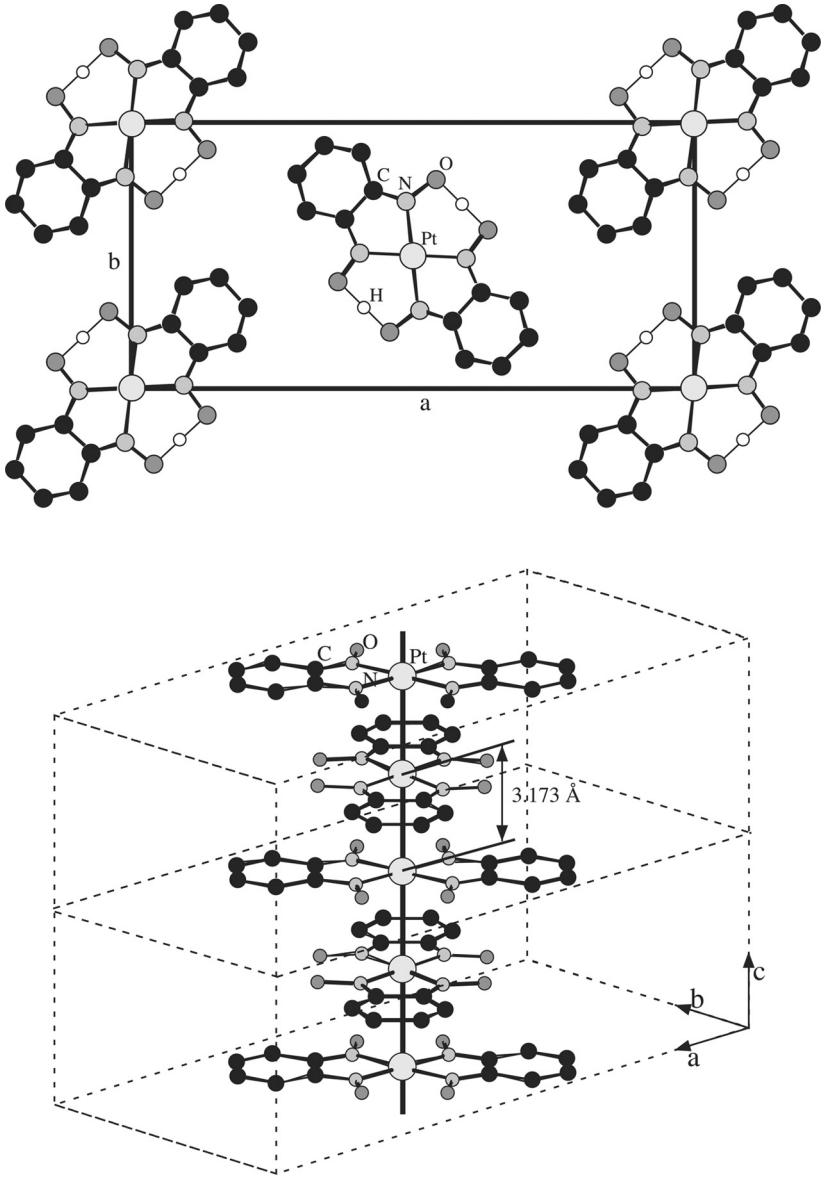

FIGURE 1 Crystal structure of $Pt(bqd)_2$ at ambient pressure.

especially shows the very large shift at the rate of $-3000\,cm^{-1}$/GPa in the low pressure region [2]. A remarkable decrease in the electrical resistance for bis-(dimethylglyoximato)platinum(II), $Pt(dmg)_2$, has been observed at high pressures [3]. Interesting pressure-induced insulator-to-metal-to-insulator (IMI) transitions for $Pt(dmg)_2$ have been studied in detail [4].

Figure 1 shows a crystal structure of bis(1,2-benzoquinonedioximato) platinum(II), $Pt(bqd)_2$, at ambient pressure. $Pt(bqd)_2$ has an orthorhombic structure with the space group Ibam and crystallizes in linear metal chain columnar structures along the c-axis. The columns are formed by square-planar complex molecules with a Pt–Pt distance of 3.17 Å in the direction of the stack [5]. The resistivities of this complex are $3 \times 10^2\,\Omega\,cm$ along the needle axis of a single crystal [6] and $2 \times 10^3\,\Omega\,cm$ for the oriented film [7] at room temperature. This compound is a semiconductor with the thermal energy gap of 0.25–0.35 eV at ambient pressure. The electrical resistivity along the c-axis of the good single crystal of $Pt(bqd)_2$ decreases with increasing pressure and sharply drops at around 0.9 GPa [8]. The optical behavior of the complex has also been studied at high pressures [9]. An insulator-to-metal transition at around 0.8 GPa has been found for the single crystals of $Pt(bqd)_2$ [8,9].

By use of synchrotron radiation, powder x-ray diffraction of $Pt(dpg)_2$ and $Pt(dmg)_2$ has been studied at high pressures; lattice constants along a-, b-, and c-axis for both complexes decrease monotonically with increasing pressure up to 10 GPa [4,10]. In particular, we have found that $Pt(dpg)_2$ is very compressible and has the smallest bulk modulus [10]. The anomalous diffraction patterns in $Pt(bqd)_2$ have already observed at high pressures [11]. A one-dimensional Pd complex, α-$Pd(bqd)_2$, shows the solid phase reaction at high pressures [12].

We have studied in detail powder x-ray diffraction of $Pt(bqd)_2$ with synchrotron radiation up to 5 GPa at room temperature and found anomalous lattice constant versus pressure curves above 2 GPa. The structural behavior of $Pt(bqd)_2$ at high pressures is discussed.

EXPERIMENTAL

o-Benzoquinonedioxime(*o*-bqd) was synthesized from commercially available *o*-nitrosoaniline, which was oxidized with basic NaOCl to give *o*-nitrosobenzene. Then, it was reduced with basic $NH_2OH \cdot HCl$ in ethanol to yield *o*-bqd. $Pt(bqd)_2$ was prepared by mixing the hot water–ethanol solution containing stoichometric amounts of K_2PtCl_4 and *o*-bqd [13]. This complex is characterized by powder x-ray diffraction using CuK_α radiation and silicon as a standard. Figure 2 shows

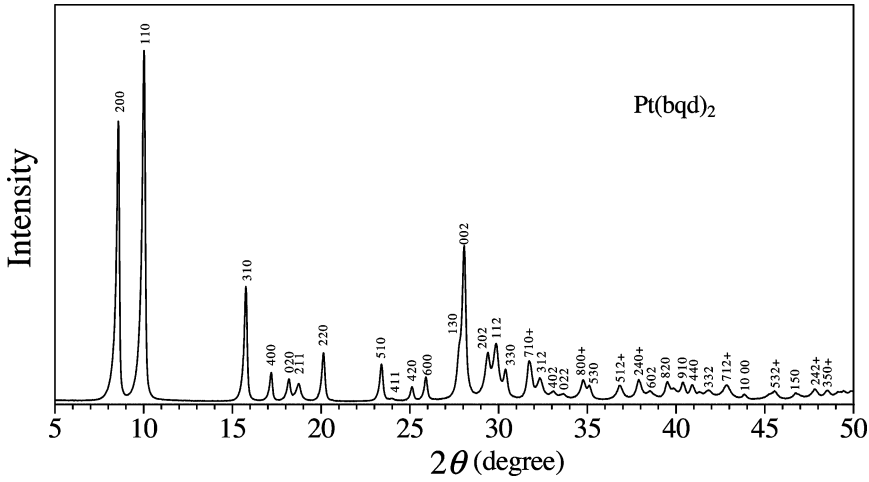

FIGURE 2 Powder x-ray diffraction pattern of $Pt(bqd)_2$ at ambient pressure.

the powder x-ray diffraction pattern of $Pt(bqd)_2$ at ambient pressure. All diffraction lines were indexed in the orthorhombic structure [5]. The crystal data obtained from these diffraction lines for $Pt(bqd)_2$ are $a = 20.654\ (3)$ Å, $b = 9.758\ (1)$ Å, $c = 6.360\ (1)$ Å, $V = 1281.9\ (4)$ Å^3, and $Z = 4$. These values almost agree with the results obtained from the single-crystal diffraction data.

By use of synchrotron radiation, powder x-ray diffraction of $Pt(pqd)_2$ was studied with a diamond-anvil cell and an imaging plate up to 6 GPa at room temperature [10]. The incident beam was monochromatized by Si(111) double crystals. The x-ray beam with a wavelength of $\lambda = 0.6199$ Å was collimated to 80 nm in diameter. High-pressure diffraction experiments were performed at the beam line (BL–18 C, proposal number: 2000G226) of the KEK Photon Factory in Tsukuba. 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. The measurement of x-ray diffraction was carried out under hydrostatic conditions because the 4:1 methanol–ethanol solution used as pressure medium was solidified at around 10 GPa.

RESULTS AND DISCUSSION

An x-ray beam of synchrotron radiation is quite suitable for a high-pressure experiment because of such excellent characteristics as brightness, a small divergence, and a constant energy. In particular,

synchrotron radiation is available for x-ray study of organic compounds consisting of the complex molecules at high pressure. Lattice parameters of ordinary one-dimensional Pt complexes such as $Pt(dmg)_2$ and $Pt(dpg)_2$ are very sensitive to pressure but decrease monotonically with increasing pressure [4,10].

Figure 3 shows powder x-ray diffraction patterns of $Pt(bqd)_2$ at high pressures. Two very strong diffraction lines, 110 and 200, of the complex are observed in the low-angle region. Both strong lines are cut because there are many weak diffraction lines in the high-angle region. Many diffraction lines shift to the high-angle region with increasing pressure. Each line shows the different pressure shift. The diffraction patterns of $Pt(bqd)_2$ do not essentially change at high pressures. Thus, the pressure-induced phase transition is not observed at room temperature. When pressure is reduced from 5 GPa to the ambient pressure, the diffraction pattern at normal pressure appears again at room temperature. This behavior is completely reversible. Figure 4 shows several d-value versus pressure curves for $Pt(bqd)_2$. The d-value of the 002 line agrees with the Pt–Pt distance in the linear metal chains and decreases

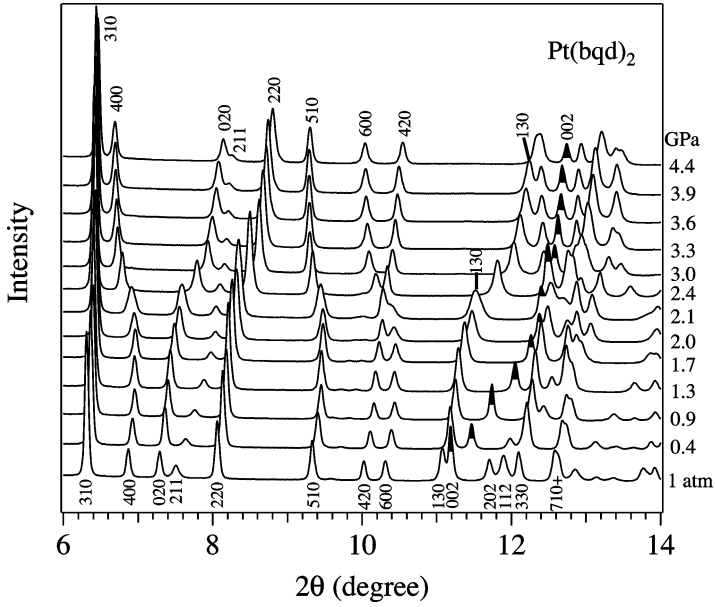

FIGURE 3 Powder x-ray diffraction patterns of $Pt(bqd)_2$ at high pressures. Because there are many diffraction lines in the high angle regions, the important 002 and 130 lines are indicated.

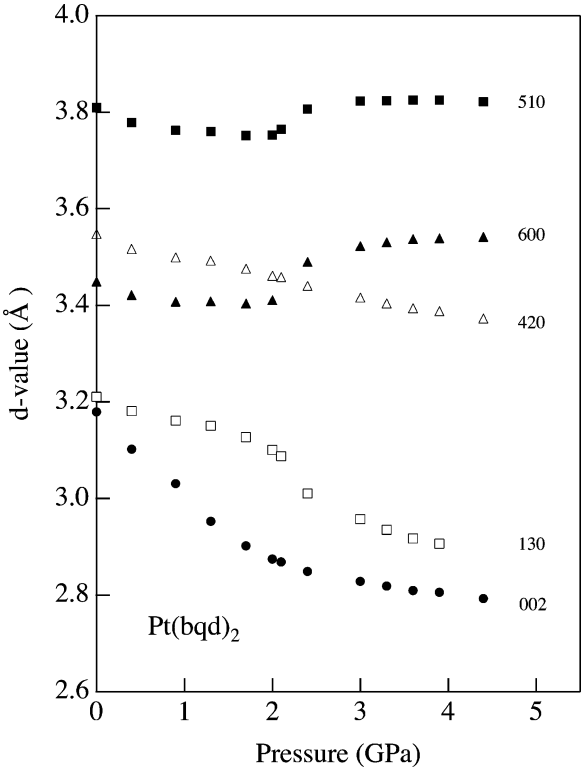

FIGURE 4 Several d-values vs. pressure curves for $Pt(bqd)_2$.

monotonically with increasing pressure. The 510 and 600 lines increase abruptly at around 2 GPa. On the contrary, the 130 line rapidly decreases at around 2 GPa. The d-value of the 420 line decreases with increasing pressure. This curve crosses to that of the 600 line at around 2 GPa. The anomalous pressure dependence of d-values was not observed for $Pt(dmg)_2$ and $Pt(dpg)_2$ [4,10].

Figure 5 shows lattice constants of $Pt(bqd)_2$ at high pressures. The c-axis monotonically decreases with increasing pressure up to 5 GPa at room temperature. On the other hand, the a- and b-axes show the anomalous behavior above 2 GPa. The a-axis increases abruptly at around 2 GPa; on the other hand, the b-axis decreases rapidly at around this pressure. Hamaya has studied x-ray diffraction of a single crystal of $Pt(bqd)_2$ at high pressures [14]. They have also found the anomalous behavior of a- and b-axes above 2 GPa. Then, the space group does not change at high pressure. The ratios of a- and b-axes, a/b, for $Pt(bqd)_2$ are 2.123 at ambient pressure and 2.434 at

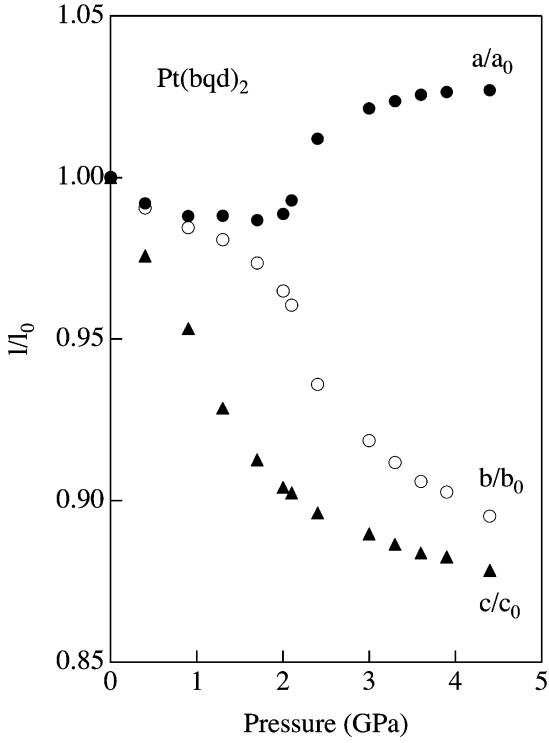

FIGURE 5 Lattice constants of $Pt(bqd)_2$ at high pressures.

4.4 GPa. Thus, the crystal structure of $Pt(bqd)_2$ becomes more anisotropic at higher pressures. The anomalous structural behavior like that for $Pt(bqd)_2$ is not observed for $Pt(dmg)_2$ [4] and $Pt(dpg)_2$ [10] at high pressures. Figure 6a and b show short contacts between C and O atoms of the adjacent molecules for $Pt(bqd)_2$ and $Pt(dmg)_2$ in the ab-plane at ambient pressure. The shortest C···O distance between the adjacent molecules along the b-axis is 3.332 Å for $Pt(bqd)_2$. If molecular arrangements in a unit cell do not change at high pressure, we can estimate that this C···O distance decreases from 3.332 Å at ambient pressure to 2.756 Å at 2.4 GPa. This distance at 2.4 GPa is much shorter than sum of van der Waals radii of C and O atoms (3.10 Å). Thus, the intermolecular interactions along the b-axis become stronger with increasing pressure. In contrast, the distance between C and O atoms in the adjacent chains increases from 3.530 Å at ambient pressure to 3.592 Å at 2.4 GPa. By applied pressure, the difference between both C···O distances becomes larger with pressure. Thus,

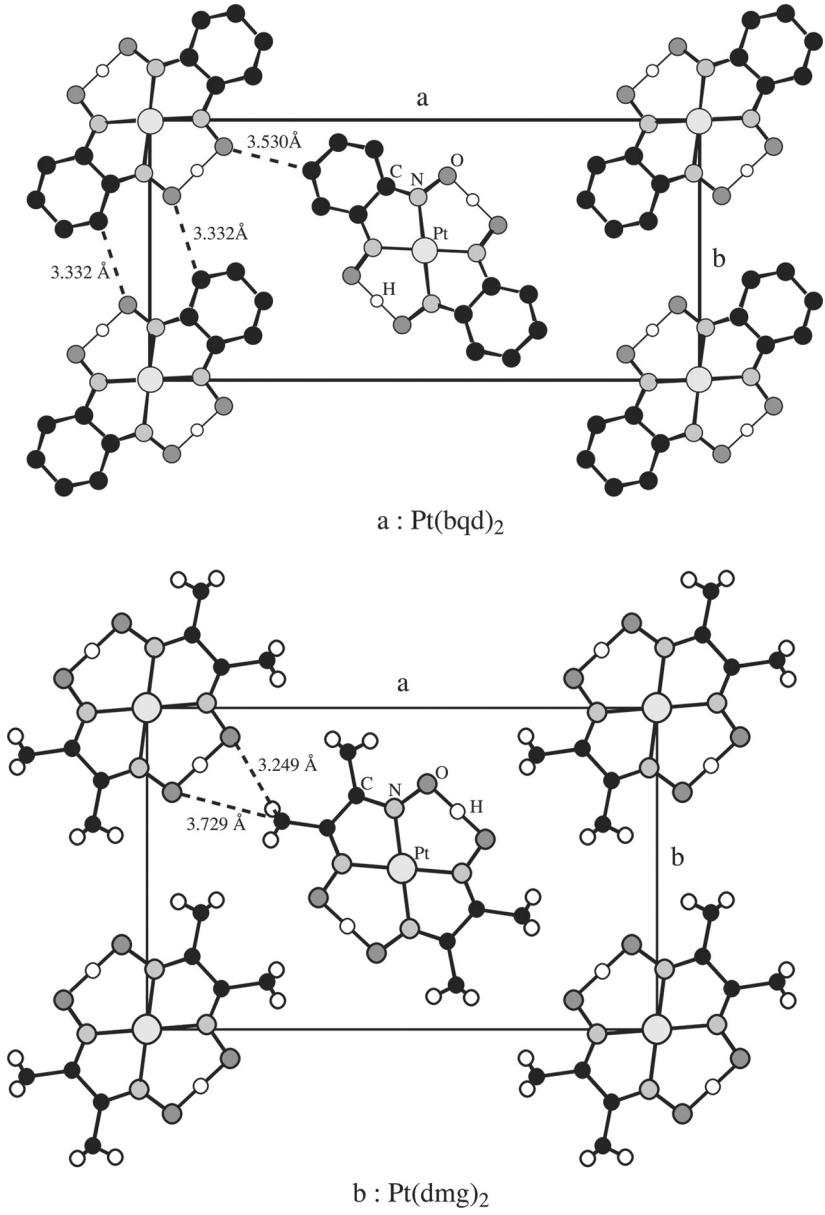

FIGURE 6 Short contacts between C and O atoms in adjacent molecules for $Pt(bqd)_2$ and $Pt(dmg)_2$ at ambient pressure.

$Pt(bqd)_2$ molecules must receive the asymmetric intermolecular interactions at higher pressures. The electrical resistivity of a polycrystal of $Pt(bqd)_2$ increases with increasing pressure above 2.4 GPa [11]. The pressure-induced absorption band of this complex is clearly observed at around 3.2 GPa [3]. We suggest that these electrical and optical properties are closely related to the asymmetric intermolecular interactions at higher pressures.

The x-ray diffractions of one-dimensional Pt complexes, $Pt(dmg)_2$ and $Pt(dpg)_2$, have already been studied at high pressures [10,15]. Lattice constants and a/b of $Pt(bqd)_2$, $Pt(dmg)_2$, and $Pt(dpg)_2$ are summarized in Table 1. Lattice constant versus pressure curves for $Pt(dmg)_2$ and $Pt(dpg)_2$ decrease monotonically with increasing pressure. The structural behavior of both complexes is very different to that of $Pt(bqd)_2$ at high pressures. The ratio of the a- and b-axes for $Pt(dmg)_2$ and $Pt(dpg)_2$ is much smaller than 2.123 of $Pt(bqd)_2$. The shortest contacts between C and O atoms are in the adjacent chain for $Pt(dmg)_2$ and $Pt(dpg)_2$. As mentioned previously, $Pt(bqd)_2$ has the shortest contact between C and O atoms along the b-axis. The C···O distance between the adjacent chains for $Pt(bqd)_2$ increases with increasing pressure. The asymmetric intermolecular interactions for $Pt(bqd)_2$ are stronger compared with those of $Pt(dmg)_2$ and $Pt(dpg)_2$.

α-$Pd(bqd)_2$ is isostructural with $Pt(bqd)_2$. The lattice constants of α-$Pd(bqd)_2$ are a = 20.649 Å, b = 9.728 Å, and c = 6.405 Å [16] and are very close to lattice parameters of $Pt(bqd)_2$. The ratio of the lattice constants, a/b, is 2.123 for α-$Pd(bqd)_2$. This value agrees with that of $Pt(bqd)_2$. The powder x-ray diffraction of α-$Pd(bqd)_2$ has been studied with synchrotron radiation at high pressures [12]. The intensity of many diffraction lines rapidly decreases with increasing pressure above 3.5 GPa. Then, the amorphous patterns are observed above 6.8 GPa. When the pressure is reduced to ambient pressure, the amorphous

TABLE 1 Lattice Constants and a/b of Three Pt Complexes at Ambient Pressure

	$Pt(bqd)_2$	$Pt(dmg)_2$	$Pt(dpg)_2$
a (Å)	20.68[a]	16.774[b]	22.829[c]
b (Å)	9.743	10.579	15.459
c (Å)	6.346	6.518	7.011
a/b	2.123	1.586	1.477

[a]Ref. 5.
[b]Ref. 14.
[c]Ref. 10.

pattern remains. This x-ray behavior is irreversible. The absorption band based on the 4d–5p transition fades out above 6 GPa. The electrical resistivity increases rapidly with time at higher pressures [12]. These electrical, optical, and structural properties at high pressure arise from the pressure-induced solid phase reaction. α-Pd(bqd)$_2$ has the shortest contacts between C and O atoms along the b-axis. The C$\cdots$O distance between the adjacent chains in this complex is similar to that of Pt(bqd)$_2$. We suggest that the solid-phase reaction for α-Pd(bqd)$_2$ is induced by the increase of asymmetric intermolecular interactions at higher pressures. On the other hand, Pt(bqd)$_2$ does not show the solid-phase reaction below 10 GPa [11]. However, the solid-phase reaction for Pt(bqd)$_2$ must be induced at higher pressures.

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