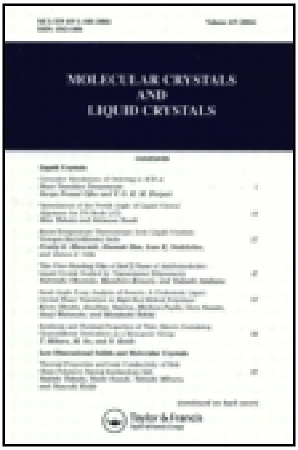

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X-ray Study with Synchrotron Radiation for One-Dimensional Complex bis(Diphenylglyoximato)-platinum(II), $Pt(DPG)_2$ at High Pressures

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X-ray Study with Synchrotron Radiation for One-Dimensional Complex bis(Diphenylglyoximato)-platinum(II), Pt(DPG)$_2$ at High Pressures

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By use of synchrotron radiation, the powder x-ray diffraction of the one-dimensional complex bis(diphenylglyoximato)platinum(II), Pt(dpg)$_2$, has been studied at room temperature and at high pressures. The lattice constants with an orthorhombic structure for Pt(dpg)$_2$, monotonically decreases with increasing pressure up to 10 GPa; the linear compressibility of each axis is estimated. The magnitude of the linear compressibility increases in the order $c > a > b$. The Pt–Pt distance along the c axis abruptly decreases from 3.50 Å at ambient pressure to 2.80 Å at around 10 GPa. A bulk modulus of Pt(dpg)$_2$, has been obtained from the volume vs. pressure curve fitted by a Birch equation of state. The bulk modulus of this complex is very small, 7.6 GPa. Pt(dpg)$_2$ is the most compressible compound. The electrical and optical properties of Pt(dpg)$_2$ are very sensitive to pressure. These interesting behaviors at high pressure are closely related to the rapid shrinkage of the c axis with increasing pressure.

Keywords: electrical and optical properties; high pressure; one-dimensional platinum complex; synchrotron radiation; x-ray diffraction

INTRODUCTION

The interesting electrical and optical behaviors of one-dimensional d^8-platinum(II) complexes with various kinds of dionedioxime ligands have been observed at high pressures [1,2]. The electrical resistivity of bis(dimethylglyoximato)platinum(II), Pt(dmg)$_2$, drastically decreases

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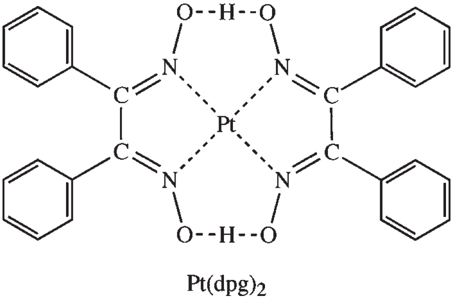

FIGURE 1 Molecular structure of Pt(dpg)$_2$.

with increasing pressure up to 6.5 GPa. The insulator-to-metal-to-insulator (IMI) transitions for this complex occur at high pressures [3,4]. The similar IMI transitions for bis(1,2-benzoquinonedioximato)-platinum(II), Pt(bqd)$_2$, are also observed at around 0.8 GPa [5,6]. The powder x-ray diffraction of Pt(dmg)$_2$ and Pt(bqd)$_2$ has been studied with synchrotron radiation at high pressures; the lattice constant along the one-dimensional metal chain (c axis) for both complexes is very sensitive to pressure [4,5].

We have already found a pressure-sensitive platinum complex, bis(diphenyl-glyoximato)platinum(II), Pt(dpg)$_2$ [7]. Figure 1 shows the molecular structure of Pt(dpg)$_2$. The absorption band of Pt(dpg)$_2$ shifts abruptly to the longer wavelength region. Then, the color of the complex remarkably turns from red-brown at ambient pressure through brown to green to greenish yellow to yellow at 2 GPa. The complex can be utilized as a pressure indicator. The shear-stress effects on the electronic spectra of Pt(dpg)$_2$ have recently been studied at high pressure. We have found that the electronic states of Pt(dpg)$_2$ remarkably change by applying shear deformation [8].

Figure 2 shows a crystal structure of Pt(dpg)$_2$ at ambient pressure. Pt(dpg)$_2$ has an orthorhombic structure with the space group, Ibam [9]. Pt(dpg)$_2$ crystallizes in linear, metal chain columnar structures along the needle axis. The columns are formed by square-planar complex molecules with a Pt-Pt distance of 3.50 Å in the direction of the stack. Because the Pt-Pt distance in the complex is very long, it is expected that the lattice constant along the c axis remarkably decreases with increasing pressure.

By use of synchrotron radiation, we have studied the powder x-ray diffraction of Pt(dpg)$_2$ up to 10 GPa at room temperature, and obtained very large linear and bulk compressibilities. The relationship between

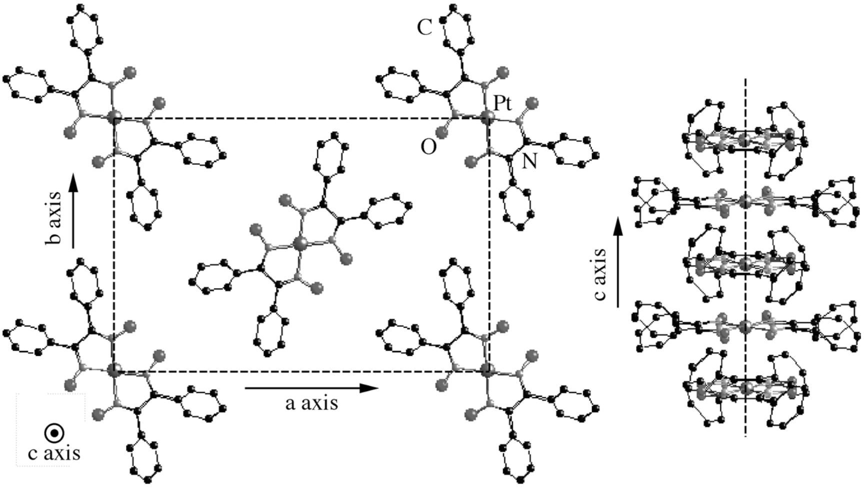

FIGURE 2 Crystal structure of one-dimensional platinum complex, Pt(dpg)$_2$.

the electrical and optical properties and the Pt-Pt distance is also discussed for one-dimensional complex, Pt(dpg)$_2$.

EXPERIMENTAL

Pt(dpg)$_2$ was prepared by mixing the hot water–ethanol solution containing stoichiometric amounts of K_2PtCl_4 and diphenylglyoxime [7]. The products were purified by repeated recrystallization from N,N-dimethylformamide or dichlorobenzene. The powder x-ray diffraction pattern of Pt(dpg)$_2$ was measured with synchrotron radiation at ambient pressure and at room temperature. Figure 3 shows the powder x-ray diffraction pattern of the complex at ambient pressure. All diffraction lines were indexed in the orthorhombic structure [9]. The crystal data obtained from these diffraction lines for Pt(dpg)$_2$ are $a = 22.829\,(1)$ Å, $b = 15.4591\,(9)$ Å, $c = 7.0114\,(3)$ Å, $V = 2474.5\,(2)$ Å^3, $Z = 4$, and $d = 1.809\,\mathrm{g/cm^3}$.

The electrical resistivity of polycrystalline Pt(dpg)$_2$ was measured as a function of pressure up to 20 GPa at room temperature [10]. The absorption spectra of a thin film of Pt(dpg)$_2$ were measured in detail measured with a sapphire-anvil cell up to 1.5 GPa under hydrostatic conditions [8].

By use of synchrotron radiation, the powder x-ray diffraction of Pt(dpg)$_2$ was studied with the diamond-anvil cell and the imaging plate up to 10 GPa at room temperature [4]. The incident beam was

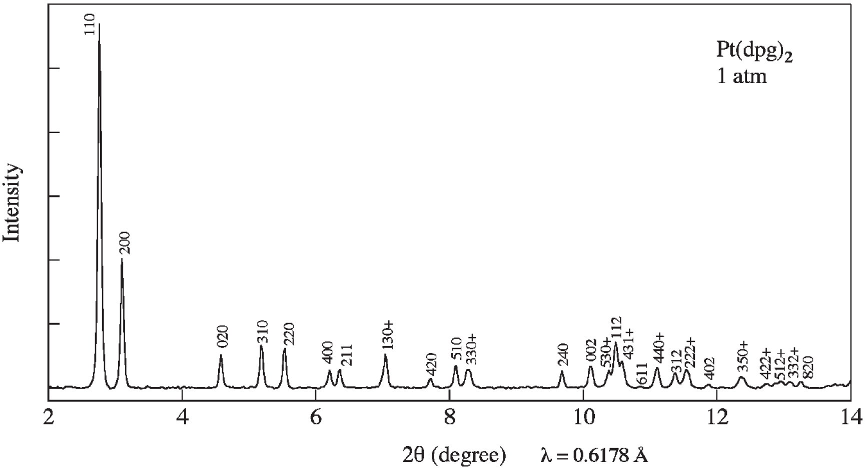

FIGURE 3 Powder x-ray diffraction pattern of $Pt(dpg)_2$ at ambient pressure.

monochromatized by Si (111) double crystals. The x-ray beam with a wavelength of $\lambda = 0.6178\,\text{Å}$ was collimated to 40 nm in diameter. High-pressure diffraction experiments were performed at the beam line (BL –18°C) 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-anvil cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby. The measurement of the 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

Electrical and Optical Properties of $Pt(dpg)_2$ at High Pressure

$Pt(dpg)_2$ has two absorption bands at 380 and 550 nm in the visible region. The 380-nm band is ascribed to the metal-to-ligand charge-transfer (M-L) transition, and the 550-nm band is due to the $5d_{z2}$-$6p_z$ transition in the central metal [7]. Figure 4 shows the wavenumber vs. pressure curve for the d-p band of $Pt(dpg)_2$. This absorption band of the complex rapidly shifts to a lower-energy region with increasing pressure. The average pressure shift between 0 and 1.5 GPa is at the rate of $-3700\,\text{cm}^{-1}/\text{GPa}$, largest among the known one-dimensional metal complexes. Figure 5 shows the resistivity vs. pressure curve for $Pt(dpg)_2$ at room temperature. This complex is an insulator with

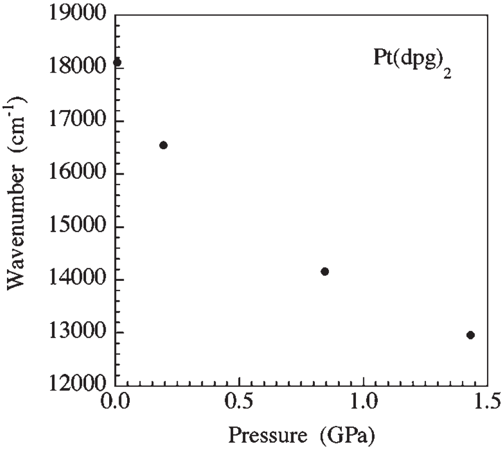

FIGURE 4 Wavenumber vs. pressure curve for the d-p band of Pt(dpg)$_2$. The absorption spectra were measured in detail with a sapphire-anvil cell in the low-pressure region.

the resistivity of greater than $10^{15}\,\Omega$ cm at ambient pressure. The resistivity of the complex abruptly decreases with increasing pressure up to 12 GPa. However, the resistivity is insensitive to pressure greater than 12 GPa. The lowest resistivity of the complex is $5 \times 10^2\,\Omega$ cm at around 20 GPa.

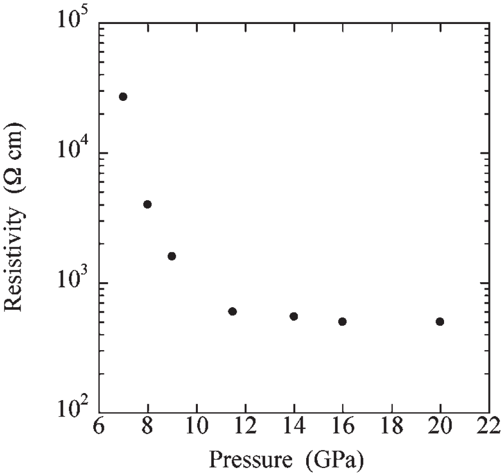

FIGURE 5 Resistivity of Pt(dpg)$_2$ at high pressures.

X-ray Diffraction at High Pressure

Figure 6 shows powder x-ray diffraction patterns of $Pt(dpg)_2$ 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. These 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 metal chains. This line is very sensitive to pressure. The powder x-ray diffraction patterns of $Pt(dpg)_2$ basically do not change up 10 GPa although the diffraction lines shift and the width broadens 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 7 shows the ratio of lattice constants (L/L_0, where L_0 = the value at ambient pressure) vs. pressure curve for $Pt(dpg)_2$. As shown in Figure 2, the crystal structure of the complex is anisotropic. The lattice constants of each axis show the different pressure dependence. These experimental data can be fitted by a quadratic equation of state:

$$L/L_0 = 1 + \mathrm{K}_{0\mathrm{L}}P + \mathrm{K}'_{\mathrm{L}}P^2 \tag{1}$$

where $\mathrm{K}_{0\mathrm{L}}$ is the linear compressibility of each axis and P is the pressure. The magnitude of the linear compressibility increases in the order

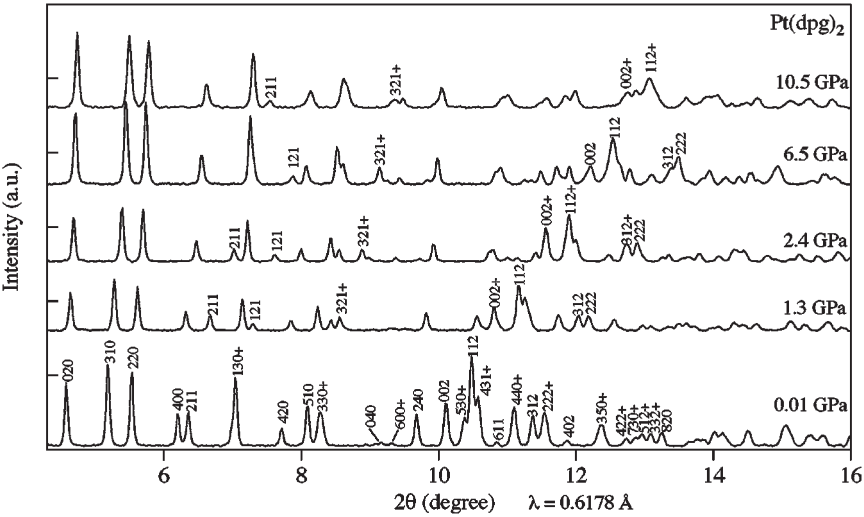

FIGURE 6 Powder x-ray diffraction patterns of $Pt(dpg)_2$ at high pressures.

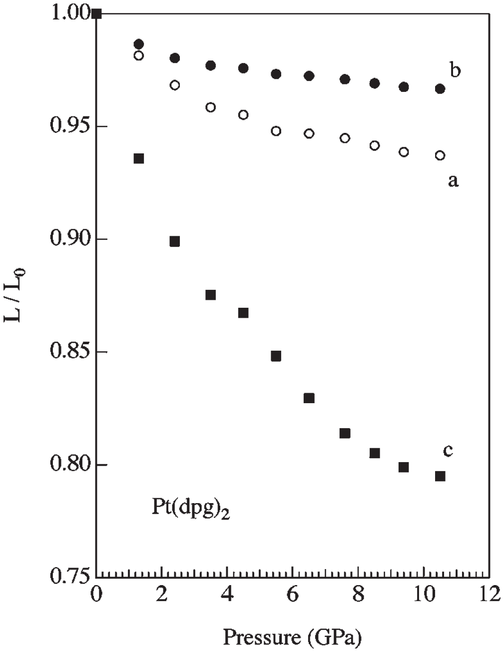

FIGURE 7 Ratio of lattice constants (L/L_0, where $L_0 =$ the value at ambient pressure) vs. pressure curves for Pt(dpg)$_2$.

c > a > b. Because there are four bulky phenyl groups in a Pt(dpg)$_2$ molecule, the intermolecular interactions in the a-b plane are very large in the crystal. Thus, the lattice constants along a and b axes are not sensitive to pressure. On the other hand, the c axis is very compressible. Bis(dimethylglyoximato)platinum(II), Pt(dmg)$_2$, is isostructural with Pt(dpg)$_2$ [11]. We have already studied the powder x-ray diffraction of Pt(dmg)$_2$ with synchrotron radiation at high pressures [4]. The values of the lattice constant and the linear compressibility for Pt(dpg)$_2$ and Pt(dmg)$_2$ are summarized in Table 1. The c axis of Pt(dpg)$_2$ is more shrinkable than that of Pt(dmg)$_2$. On the contrary, a and b axes of Pt(dpg)$_2$ are less compressible compared with those of Pt(dmg)$_2$.

The Pt-Pt distances (a half of the c axis) are 3.50 Å for Pt(dpg)$_2$ and 3.26 Å for Pt(dmg)$_2$ at ambient pressure. These distances of both complexes decrease rapidly from the values at ambient pressure to 2.85 Å at around 7 GPa for Pt(dpg)$_2$ and at around 5 GPa for Pt(dmg)$_2$. This distance almost agrees with the Pt-Pt spacing of the one-dimensional metal, $K_2Pt(CN)_4Br_{0.3}3H_2O$ [12].

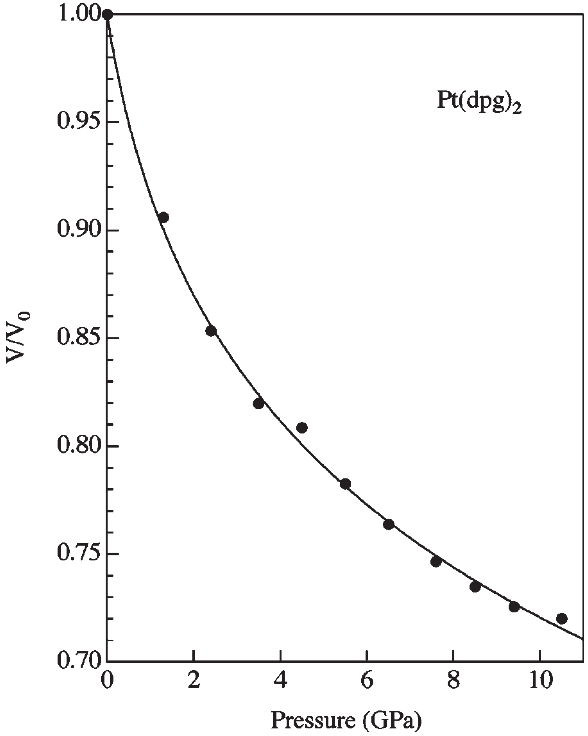

FIGURE 8 Relative cell volume (V/V_0) vs. pressure curve for Pt(dpg)$_2$.

Using the diamond-anvil cell, we have measured the absorption spectra of Pt(dpg)$_2$ at higher pressures. The average pressure shift of the d-p band for Pt(dpg)$_2$ is at the rate of $-3000\,\mathrm{cm}^{-1}/\mathrm{GPa}$ in the 0–2 GPa region. On the other hand, the 680-nm band ascribed to the

TABLE 1 Lattice Constant, Linear Compressibility (K_{0L}), and Bulk Compressibility (K_0) for Pt(dpg)$_2$ and Pt(dmg)$_2$

Constant	Pt(dpg)$_2$	Pt(dmg)$_2$
a (Å)	22.829	16.7735
b (Å)	15.4591	10.5790
c (Å)	7.0114	6.5175
d (g/cm^3)	1.809	2.443
K_{0a} (GPa^{-1})	0.0134(6)	0.0190(4)
K_{0b} (GPa^{-1})	0.0075(6)	0.0158(7)
K_{0c} (GPa^{-1})	0.040(2)	0.0312(8)
K_0 (GPa^{-1})	0.132	0.1

d-p transition for $Pt(dmg)_2$ shifts to longer wavelength at rate of $-2600\,cm^{-1}/GPa$ [4]. The Pt-Pt distances in both Pt complexes rapidly decrease with increasing pressure. The large pressure shift of the absorption band mainly arises from the abrupt decrease of the Pt-Pt distance (c axis). It is expected that the optical energy gap of both complexes become zero at around 7 GPa for $Pt(dpg)_2$ and 5 GPa for $Pt(dmg)_2$.

As shown in Figure 5, the resistivity of $Pt(dpg)_2$ decreases sharply with increasing pressure. The resistivity at around 7 GPa of the metallic behavior is expected to be about $10^4\,\Omega\,cm$. The metallic behavior in $Pt(dpg)_2$ is not observed up to 20 GPa. In contrast, $Pt(dmg)_2$ shows the insulator-to-metal transition at around 5 GPa [3,4]. The ratios of the lattice constant, a/c and b/c, are 3.26 and 2.20 for $Pt(dpg)_2$, and 2.57 and 1.63 for $Pt(dmg)_2$. The structure of $Pt(dpg)_2$ is more anisotropic compared with that of $Pt(dmg)_2$. There is the short contact between C and O atoms in the adjacent chains for $Pt(dmg)_2$ at high pressures [11]. Thus, this complex must have fairly two-dimensional character at high pressures. We suggest that the electrical behavior of the Pt complexes at high pressure is closely related to the anisotropic crystal structure.

Figure 8 shows the relative cell volume (V/V_0) vs. pressure curve for $Pt(dpg)_2$. The cell volume monotonically decreases with increasing pressure up to 10 GPa. The experimental data can be fitted by a Birch equation of state [13]:

$$P = (3/2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 - 3/4(4 - B_0')[(V/V_0)^{-2/3} - 1]\} \tag{2}$$

where B_0 is the bulk modulus, B_0' its first pressure derivative, V the volume, and P the pressure. A least-squares fit to the data of $Pt(dpg)_2$

TABLE 2 Bulk Modulus and Crystal Structure of Various Materials

Compound	Structure	B_0 (GPa)
$Pt(dpg)_2$	orthorhombic	7.6
$Pt(dmg)_2$	orthorhombic	10.0
C_{60}	cubic	18.1
NaCl	cubic	24
KCl	cubic	17
MgO	cubic	225
Al_2O_3	hexagonal	252
Si	cubic	98
Diamond	cubic	441

gives the following values: $B_0 = 7.6 \pm 1\,\text{GPa}$ and $B_0' = 10.0 \pm 1.6$. The bulk modulus is defined as follows: $B_0 = -V_0 \mathrm{d}P/\mathrm{d}V$. The bulk compressibility (K_0) is $K_0 = 1/B_0$. The bulk modulus and its pressure derivative of $\mathrm{Pt(dmg)_2}$ are $B_0 = 10.0 \pm 0.5$, $B_0' = 7.2 \pm 0.5$, respectively. The densities of $\mathrm{Pt(dpg)_2}$ and $\mathrm{Pt(dmg)_2}$ are 1.809 and $2.443\,\mathrm{g/cm^3}$, respectively. The crystal packing of $\mathrm{Pt(dpg)_2}$ is very loose because of the existence of bulky phenyl groups. Thus, the bulk modulus of $\mathrm{Pt(dpg)_2}$ is smaller than that of $\mathrm{Pt(dmg)_2}$. Bulk moduli and crystal structures of various materials are summarized in Table 2. The bulk modulus of the oxides and the covalent crystals is very large. Ionic crystals such as alkali halides have a small bulk modulus. Molecular crystals have a smaller bulk modulus compared with these ionic crystals. The bulk modulus of $\mathrm{Pt(dpg)_2}$ is smallest among these materials, below 1/3 of NaCl. Thus, $\mathrm{Pt(dpg)_2}$ is the most compressible compound.

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