12. Pressure-sensitive Optical Properties of Bis (1, 2-dionedioximato)-Palladium (II) Complexes

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Abstract: The absorption spectra of Pd(niox)₂, Pd(dmgo)₂ and Pd(dpg)₂ have been studied at high pressures. The absorption bands based on the 4d_{z²}-5p_z transition shifted rapidly to longer wavelengths with increasing pressure. The mean rates of the red shift with pressure were ca. -1170 cm⁻¹/GPa for Pd(niox)₂, ca. -1300 cm⁻¹/GPa for Pd(dmgo)₂ and ca. -1990 cm⁻¹/GPa for Pd(dpg)₂. A new pressure-induced absorption band at around 410 nm was observed for Pd(niox)₂ above 10 GPa. The electronic states of the palladium complexes are discussed. The colors of the complexes in the diamond-anvil pressure cell were observed visually at various pressures. The colors of the complexes turn from yellow to orange and then to successive colors in the visible spectrum with increasing pressure. These materials can be utilized as a pressure indicator over the wide pressure range.

Key words: High pressure; absorption spectra; palladium complexes; pressure indicator.

Introduction. One-dimensional d⁸ metal complexes with various kinds of 1,2-dionedioximes show interesting electrical and optical properties at high pressures.¹⁾⁻⁴⁾ Pressure-induced insulator-to-metal-to-semiconductor transitions and pressure-induced absorption bands for the platinum complexes have been found at room temperature.^{3),4)} The interesting spectral features at high pressure have also been observed for the nickel complexes.⁵⁾

Bis(1,2-dionedioximato)metal(II)(Ni, Pd, Pt) complexes have various fine colors at atmospheric pressure. The absorption bands of these complexes shift rapidly to longer wavelengths with increasing pressure. Thus, the colors of these complexes remarkably change with the pressure shift of the absorption bands.⁶⁾⁻⁸⁾ If the relationship between color and pressure is studied in detail, a semiquantitative value of pressure could be obtained from a visual observation of the color change with pressure. This can be utilized as a pressure indicator by a colorimetric method similar to pH testing paper.

The absorption spectra of some d⁸ palladium complexes have already been studied at high pressures.^{2),6)} A preliminary report on the high-pressure color change of bis(1,2-cyclohexanedionedioximato)palladium(II)[1,2-cyclohexanedionedioxime is usually called nioxime], Pd(niox)₂, has been given in a previous paper.⁶⁾ Fig. 1 shows the molecular structures of three bis(1,2-dionedioximato)palladium(II) complexes. In this paper, we report the results of the optical properties of these complexes and discuss their electronic states, and further, discuss about an application as the pressure indicator.

Experimental. The development of diamond-anvil pressure cells enables the effect of the pressure on various materials to be observed in situ. Using this cell, photographs of the

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Fig. 1. Molecular structures of bis(1,2-dionedioximato)palladium(II): a) bis(dimethylglyoximate)palladium(II), Pd(dmg)_2 , b) bis(diphenylglyoximate)palladium(II), Pd(dpg)_2 , c) bis(1,2-cyclohexanedionedioximate)palladium(II), Pd(niox)_2 .

palladium complexes were taken at various pressures. The absorption spectra of the complex were measured simultaneously at high pressures. An optical system consisted of a standard microscope and a monochromator with an associated photodetection system.⁸⁾ Pressure was determined from pressure shift in the sharp R-line fluorescence spectrum of ruby.⁹⁾ Water was used as the pressure-transmitting medium.

The palladium complexes shown in Fig. 1 were prepared from an aqueous solution of K_2PdCl_4 and a hot alcoholic solution of the 1,2-dionedioximes. These compounds used in this experiment are dimethylglyoxime, 1,2-cyclohexanedionedioxime(nioxime) and diphenylglyoxime. The d^8 complexes prepared were purified by recrystallization.

Results and discussion. Fig. 2 shows the absorption spectra of thin films of Pd(niox)_2 , Pd(dmg)_2 and Pd(dpg)_2 . The thin films of these complexes were prepared by evaporation onto a substrate in a vacuum of ca. 10^{-6} Torr.¹⁰⁾ A thickness of the film was about 1000 Å. The absorption spectrum in the film of Pd(dpg)_2 is similar to that of Pt(dpg)_2 . The absorption band of Pt(dpg)_2 is already assigned by us.⁸⁾ Thus, the 280, 347 and 436 nm bands of Pd(dpg)_2 are ascribed to the $\pi\text{-}\pi^*$ transition in the ligand, the metal-to-ligand

Fig. 2. Absorption spectra of thin films of Pd(niox)_2 , Pd(dmg)_2 and Pd(dpg)_2 .

Fig. 3a and 3b. Absorption spectra of polycrystal of $\text{Pd}(\text{niox})_2$ at high pressures.

charge transfer (M-L) transition and the $4d_{z^2}-5p_z$ transition, respectively. Two absorption bands of $\text{Pd}(\text{dmg})_2$ were located at around 290 and 461 nm in the 250–600 nm region. The absorption spectrum of $\text{Pd}(\text{dmg})_2$ has already been studied at atmospheric pressure.¹¹⁾ The 290 nm band is ascribed to $\pi-\pi^*$ transition in the ligand. The 461 nm band was assigned to $4d-5p$ transition. The absorption spectrum of $\text{Pd}(\text{niox})_2$ is similar to that of $\text{Pd}(\text{dmg})_2$. The interesting spectral features were observed for both complexes; the absorption band based on the M-L transition disappeared at atmospheric pressure. The M-L band is found for the nickel and platinum complexes. Especially, the absorption intensity of the M-L band of $\text{Ni}(\text{dmg})_2$ and $\text{Ni}(\text{niox})_2$ is strong compared with the platinum complexes.⁵⁾

Fig. 3a and 3b show the absorption spectra of $\text{Pd}(\text{niox})_2$ in the visible region at high pressures. The polycrystalline sample was used in this experiment. The absorption peak of the polycrystal of $\text{Pd}(\text{niox})_2$ is about 10 nm shorter than that of the thin film. The d-p band at around 465 nm shifted remarkably to longer wavelengths with increasing pressure. The absorption peak was not located in the visible region above 7 GPa. A new absorption band at around 410 nm appeared above 10 GPa. This band is not due to the pressure shift of the 290 nm band because the absorption intensity is very weak. The absorption intensity of the M-L band is generally weak for bis(1,2-dionedioximato)metal(II) complexes. Thus, the new band at around 410 nm may arise from the M-L band induced by pressure.

The sample in the diamond-anvil cell was visually observed at high pressures. The color of $\text{Pd}(\text{niox})_2$ changed markedly with pressure shift of the band. Plate 1 shows a series of photographs of the sample at various pressures. The color of $\text{Pd}(\text{niox})_2$ turned from yellow (at atmospheric pressure) to orange (at 1.4 GPa), to red (at 2.3 GPa) to purple (at 3.3 GPa), to blue (at 4.5 GPa), to green (at 5.9 GPa), and pale yellow (at 8 GPa) with

Fig. 4. The relation between the wavelength of the absorption peak and pressure for $\text{Pd}(\text{niox})_2$. The colors are shown in the Figure.

Plate 1. A series of photographs shows the color of $\text{Pd}(\text{niox})_2$ at various pressures: a) 0.4 GPa, b) 3 GPa, c) 4.5 GPa, d) 5.9 GPa, e) 10.1 GPa, f) the line drawing identifying the position of the sample and two reference rubies. The aperture in the gasket measures 0.3 mm from side to side. The colors at various pressures correspond to the absorption spectra shown in Fig. 3a and 3b.

increasing pressure. Fig. 4 shows the relation between the wavelength of the absorption peak and the pressure for $\text{Pd}(\text{niox})_2$. The wavelength of the absorption peak shifted linearly to pressure. The rate is $\lambda(\text{nm}) = 39 \times P(\text{GPa}) + 453$. The color observed at various pressures are shown in Fig. 4. If the relationship between color and pressure is studied in detail, a semiquantitative value of pressure can be obtained from the visual observation of the color change with pressure. Thus, $\text{Pd}(\text{niox})_2$ can be utilized as a pressure indicator over range 0–8 GPa. It should be noted that the color tone depends on a number of factors including light source, sample thickness, pressure-transmitting medium and pressure distribution.

Fig. 5 shows the absorption spectra of a polycrystal of $\text{Pd}(\text{dmg})_2$ at high pressures. The d-p band at around 450 nm shifted remarkably to longer wavelengths with increasing pressure. The absorption spectra of $\text{Pd}(\text{dmg})_2$ are similar to those of $\text{Pd}(\text{niox})_2$ at high pressures. The absorption spectra of polycrystal of $\text{Pd}(\text{dpg})_2$ were also measured at high pressures. The d-p band at around 425 nm shifted sharply to longer wavelengths with

Fig. 5. Absorption spectra of polycrystal of Pd(dmg)_2 at high pressures.

Fig. 6. Pressure shifts of the d-p bands of three palladium complexes. The energies of the absorption peaks at atmospheric pressure are 21500 cm^{-1} for Pd(niox)_2 , 22200 cm^{-1} for Pd(dmg)_2 and 23500 cm^{-1} for Pd(dpg)_2 .

increasing pressure. Fig. 6 shows the pressure shift of the d-p band of the three palladium complexes. The mean rates of the red shift with pressure are ca. $-1170 \text{ cm}^{-1}/\text{GPa}$ for Pd(niox)_2 , ca. $-1300 \text{ cm}^{-1}/\text{GPa}$ for Pd(dmg)_2 and ca. $-1990 \text{ cm}^{-1}/\text{GPa}$ for Pd(dpg)_2 . The rates of the pressure shift increase in the order $\text{Pd(niox)}_2 < \text{Pd(dmg)}_2 < \text{Pd(dpg)}_2$. This tendency is also observed for the nickel and platinum complexes.^{5),8)}

Pd(dmg)_2 is orthorhombic, $a_0=16.9 \text{ \AA}$, $b_0=10.6 \text{ \AA}$, $c_0=6.50 \text{ \AA}$, $Z=4$, space group Ibam.¹²⁾ The lattice constants of Pd(dmg)_2 have not been studied yet at high pressures. Pt(dmg)_2 is orthorhombic, $a_0=16.774 \text{ \AA}$, $b_0=10.579 \text{ \AA}$, $c_0=6.518 \text{ \AA}$, $Z=4$, space group Ibam. Both complexes are isostructural. Using X-ray diffraction the crystal structure of Pt(dmg)_2 has been investigated at high pressures.¹³⁾ The ratios of the lattice constants at high pressures to those at atmospheric pressure (a/a_0 , b/b_0 , c/c_0) decrease rapidly with pressure. The lattice constants shrink about 9% for the c -axis (needle axis) and about 4.5% for the a - and b -axes up to 4 GPa. Since the lattice constants of Pd(dmg)_2 are very close to those of Pt(dmg)_2 , compression behavior of Pd(dmg)_2 would be expected to be similar to

Pt(dmg)₂. The c-axis of Pd(dmg)₂ would easily shrink compared with the a- and b-axes.

The polarization of the transition for the d-p band is parallel to the c-axis with Pd-Pd bonds. The d_{z²} and p_z orbitals extend in the direction of the c-axis. Thus, the d-p band shows a marked red shift with decreasing Pd-Pd distance. The d-p band of Pd(dpg)₂ showed the largest red shift with increasing pressure in the three palladium complexes. The crystal packing of Pd(dpg)₂ is very loose because of the bulky phenyl group. The complex has the largest Pd-Pd distance of 3.52 Å in three palladium complexes.¹⁴⁾ Thus, the optical properties of Pd(dpg)₂ are very sensitive to pressure.

The d-p bands of the palladium complexes are located at much shorter wavelengths compared with those of the nickel and platinum complexes at atmospheric pressure. Since the absorption bands of the palladium complexes shift from about 400 nm to 800 nm in the visible region, the color turns from yellow to orange and then to successive colors in the visible spectrum with increasing pressure. Thus, the palladium complexes become excellent pressure indicators over the wide pressure range.

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