

## Powder x-ray diffraction analysis and bulk modulus of bis(dimethylglyoximato)palladium(II) and bis(1,2-diphenylglyoximato)palladium(II) under high pressure

Keiki TAKEDA\*, Tomoya SASAKI, Junichi HAYASHI, Ichimin SHIROTANI  
Muroran Institute of Technology, 27-1, Mizumoto, Muroran-shi 050-8585, Japan

### Introduction

Interesting electrical and optical behaviors of one-dimensional bis(dimethylglyoximato)metal(II),  $M(\text{dmg})_2$  have been observed at high pressures[1-3]. The insulator-to-metal-to-insulator (IMI) transitions for Pt complexes occur at high pressures. By use of synchrotron radiation, powder x-ray diffraction of several one-dimensional metal complexes has been studied at high pressures. The M-M distance along the one-dimensional chain for  $\text{Ni}(\text{dmg})_2$  and  $\text{Pt}(\text{dmg})_2$  decreases rapidly with increasing pressure. The crystal structures of bis(1,2-diphenylglyoximato)palladium(II),  $\text{Pd}(\text{dpg})_2$ , and  $\text{Pd}(\text{dmg})_2$  are orthorhombic. The both compounds are isostructural with  $\text{Pt}(\text{dmg})_2$ . Using synchrotron radiation, we have studied powder x-ray diffraction of  $\text{Pd}(\text{dpg})_2$  and  $\text{Pd}(\text{dmg})_2$  at high pressure and room temperature.

### Experimentals

The powder x-ray diffraction of  $\text{Pd}(\text{dmg})_2$  and  $\text{Pd}(\text{dpg})_2$  was studied with a diamond-anvil cell and an imaging plate up to 20 GPa. The x-ray beam with a wavelength of  $\lambda=0.6197\text{\AA}$  was collimated to  $80\mu\text{m}$  in diameter. High pressure diffraction experiments were performed at BL-18C. A 4:1 methanol-ethanol solution was used as the hydrostatic pressure fluid. The pressure in a diamond-anvil cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby.

### Results and Discussion

The powder x-ray diffraction patterns have been measured with synchrotron radiation for  $\text{Pd}(\text{dmg})_2$  and  $\text{Pd}(\text{dpg})_2$  at high pressures. The intensity of the diffraction lines decreases and the width broaden with increasing pressure. The change of the powder x-ray diffraction patterns with the phase transition for both complexes is not observed up to 20 GPa. When pressure is reduced from 20 GPa to the ambient pressure, the diffraction patterns at normal pressure appear again at room temperature. This behavior is completely reversible. Figure 1 shows ratio of lattice constants ( $l/l_0$ ,  $l_0$ =the value at ambient pressure) and cell volume vs pressure curves for  $\text{Pd}(\text{dmg})_2$  and  $\text{Pd}(\text{dpg})_2$ . The lattice constants decrease with increasing pressure up to 10 GPa. The crystal structures of both complexes are anisotropic. The lattice constant of each axis shows the different pressure

dependence. The a-axis shows a larger decrease compared with the b-axis. The ratios of lattice constants at high pressures to those at atmospheric pressure show the largest shrinkage along the c-axis. The Pd-Pd separation within the chain for  $\text{Pd}(\text{dmg})_2$  decreases continuously from  $3.25\text{\AA}$  at ambient pressure to  $2.90\text{\AA}$  at 10GPa. The value at 10GPa is longer than the Pd-Pd bond length in the metal ( $2.75\text{\AA}$ ). The c-axis of the  $\text{Pd}(\text{dpg})_2$  shrink compared with that of  $\text{Pd}(\text{dmg})_2$ . The pressure vs. volume curves for  $\text{Pd}(\text{dmg})_2$  and  $\text{Pd}(\text{dpg})_2$  are fitted by a Birch equation of state. Bulk modulus of  $\text{Pd}(\text{dmg})_2$  and  $\text{Pd}(\text{dpg})_2$  are 9.9(7) GPa and 7.6(5) GPa, respectively. This value of  $\text{Pd}(\text{dmg})_2$  is smaller than that of  $\text{Pt}(\text{dmg})_2$ [2].

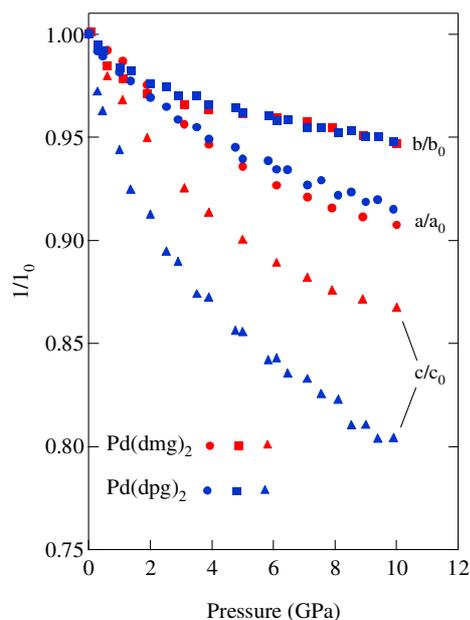


Figure 1 Ratio of lattice constant ( $l/l_0$ ) vs. pressure curves for  $\text{Pd}(\text{dmg})_2$  and  $\text{Pd}(\text{dpg})_2$  at room temperature.

### References

- [1] I. Shirovani et al., Bull. Chem. Soc. Jpn., 64, 1607 (1991).
- [2] K. Takeda et al., Chem. Mater. 12, 912(2000).
- [3] K. Takeda et al., Mol. Cryst. Liq. Cryst., 460, 131 (2006).

\* ktakeda@mmm.muroran-it.ac.jp