1078 © *1992 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *65*, *1078—1083 (1992)* [Vol. 65, No. 4

Absorption Spectra and Electrical Resistivities of Bis(1,2-dionedioximato)nickel(II) Complexes at High Pressures

Ichimin Shirotani,* Kazunaga Suzuki, Toshihiro Suzuki,†
Takehiko Yagi,† and Masashi Tanaka††
Muroran Institute of Technology, 27-1, Mizumoto, Muroran 050
†The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
††College of General Education, Nagoya University, Chikusa-ku, Nagoya 464
(Received October 21, 1991)

The absorption spectra of [Ni(dmg)$_2$], [Ni(niox)$_2$], [Ni(dpg)$_2$], and [Ni(bqd)$_2$] were studied at various pressures. Two characteristic absorption bands, the metal-to-ligand charge-transfer (M—L) and the 3d—4p bands, were observed in the visible region for these complexes. The interesting spectral features observed under high pressures were: (1) The excitations shift remarkably to lower energies with increasing pressure. (2) The rates of the peak shifts for the d—p and M—L bands increase in the order [Ni(niox)$_2$]<[Ni(dmg)$_2$]<[Ni(dpg)$_2$]. (3) The peak shifts of the M—L bands are much smaller than those of the d—p bands. (4) The absorption intensity of the M—L band of [Ni(niox)$_2$] decreases rapidly above 10 GPa, and the band is hardly observed at around 14 GPa. (5) A new absorption band in [Ni(dpg)$_2$] exists above about 3 GPa. The electrical resistivity of [Ni(dmg)$_2$], [Ni(niox)$_2$], and [Ni(dpg)$_2$] has been studied under high pressures. These complexes are insulators with a resistivity of 10^{15} Ω cm at atmospheric pressure. The resistivities at around 23 GPa were 50 Ω cm for [Ni(dmg)$_2$], 7×10^5 Ω cm for [Ni(niox)$_2$] and 2×10^3 Ω cm for [Ni(dpg)$_2$].

One-dimensional d^8 metal complexes with various kinds of 1,2-dionedioximes (Fig. 1) show interesting electrical and optical properties under high pressures.[1—5] Pressure-induced insulator-to-metal-to-semiconductor transitions and pressure-induced absorption bands for bis(1,2-dionedioximato)platinum(II) complexes have been found at room temperature.[6,7] The electrical and optical properties of d^8 metal complexes are very sensitive to any decrease in the metal-metal distance in a linear chain.

The nickel ions in square planar d^8 complexes(shown in Fig. 1) are surrounded by four nitrogen atoms of two 1,2-dionedioxime anions. The d orbitals of the nickel ion are split by a crystal field of D_{4h} symmetry. The 8 electrons of the nickel ion core fill the d_{z^2}, d_{xy}, d_{yz}, and d_{zx} states. These complexes crystallize in a columnar structure. The molecules of the complexes stack one above the other with rotation of 90°, which forms a chain with the metal-metal distance, varying from 3.2 to 3.6 Å.[8,9] The crystalline spectra of [Ni(dmg)$_2$] have been studied in the 170—800 nm region at atmospheric pressure.[10,11] Two characteristic bands in a crystalline

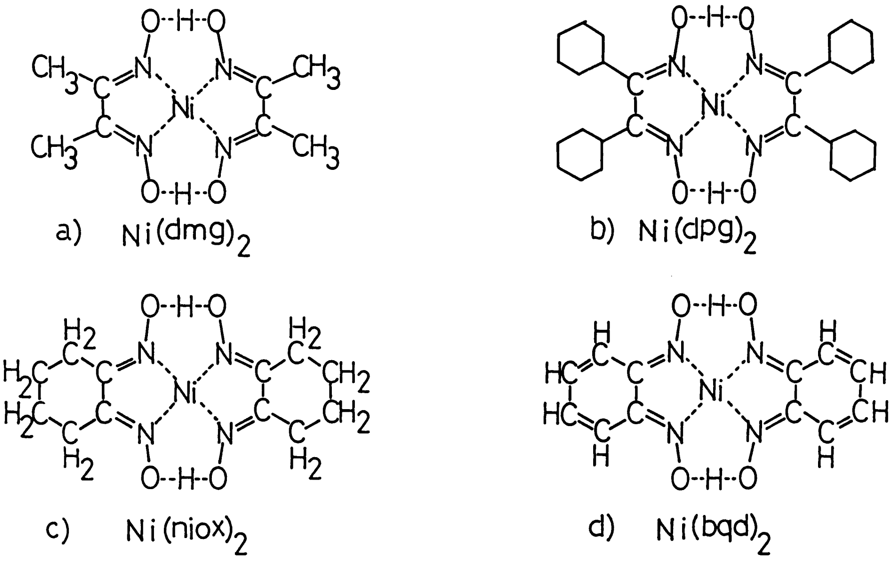

a) Ni(dmg)$_2$
b) Ni(dpg)$_2$
c) Ni(niox)$_2$
d) Ni(bqd)$_2$

Fig. 1. Molecular structures of bis(1,2-dionedioximato)nickel(II); a) bis(dimethylglyoximato)nickel(II), [Ni(dmg)$_2$], b) bis(diphenylglyoximato)nickel(II), [Ni(dpg)$_2$], c) bis(1,2-cyclohexanedionedioximato)nickel(II), [Ni(niox)$_2$](1,2-cyclohexanedionedioxime is usually called nioxime), d) bis(1,2-benzoquinonedioximato)nickel(II), [Ni(bqd)$_2$].

state were observed at around 410 and 530 nm in the visible region. The latter band is polarized parallel to a column, and is ascribed to the 3d–4p transition.[11] This band shifts rapidly to longer wavelengths with increasing pressure.[4,5] The 410 nm band is polarized perpendicular to the column and has been assigned to the metal-to-ligand charge-transfer (M–L) transition.[11] The pressure effect of this band has not yet been studied. The absorption spectra of $[Ni(niox)_2]$ and $[Ni(dpg)_2]$ have briefly been reported.[4,12]

$[Ni(dmg)_2]$ is an insulator with a resistivity of 10^{15} Ω cm at atmospheric pressure.[13] The resistivity of the complex decreases rapidly with increasing pressure in the low-pressure region, and levels off above 20 GPa.[2] The pressure shift of the d–p band tends to become level above 20 GPa.[5] Thus, the resistivity of $[Ni(dmg)_2]$ at high pressures is mainly interpreted in terms of a decrease in the band gap between filled $3d_{z^2}$ valence and $4p_z$ conduction bands with pressure. The unusual electrical behavior is observed for $[Ni(niox)_2]$ and $[Ni(dpg)_2]$ at high pressure.[2]

In this paper we present some results concerning the optical and electrical behavior in four bis(1,2-dionedioximato)nickel(II) complexes at various pressures, and discuss the electronic states of these complexes.

Experimental

The nickel complexes shown in Fig. 1 were prepared from an aqueous solution of $NiCl_2$ and a hot alcoholic solution of the 1,2-dionedioximes. The compounds used in this experiment were dimethylglyoxime (Hdmg), diphenylglyoxime (Hdpg), 1,2-cyclohexanedionedioxime [nioxime(Hniox)] and 1,2-benzoquinonedioxime (Hbqd). These complexes were purified by recrystallization from o-dichlorobenzene or dimethylformamide.

Thin films of d^8 complexes with 1,2-dionedioxime ligands can be easily prepared by evaporation onto either a quartz or glass substrate in high vacua.[14] The thickness of the film was monitored by means of a quartz-crystal oscillator. The absorption spectra of the evaporated films with thickness of 600—1000 Å were measured with a Hitachi 330-type spectrophotometer at room temperature.

A diamond-anvil pressure cell was used for measuring the absorption spectra at high pressure. The optical system comprised a stanard microscope and a monochromator with an associated photodetection system.[15] The absorption spectra at high pressure were measured in the 400—800 nm region at room temperature. The pressure was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby.[16] Water was used a pressure-transmitting medium.

Resistivity measurements at high pressure were performed using a split-sphere apparatus.[17] The electrical resistivity of the polycrystalline pellets of the nickel complexes was measured as a function of pressure at room temperature.

Results and Discussion

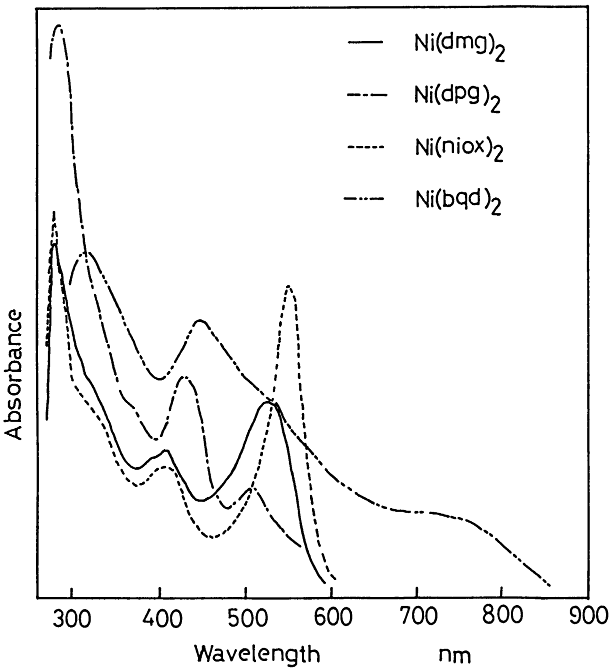


Fig. 2. Absorption spectra of thin films of bis(1,2-dionedioximato)nickel(II) complexes.

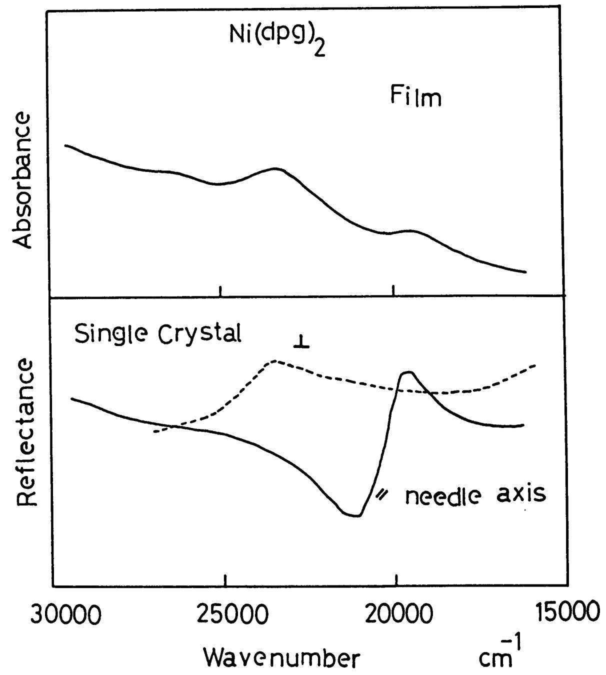


Fig. 3. Reflectance spectra of a single crystal of $[Ni(dpg)_2]$.

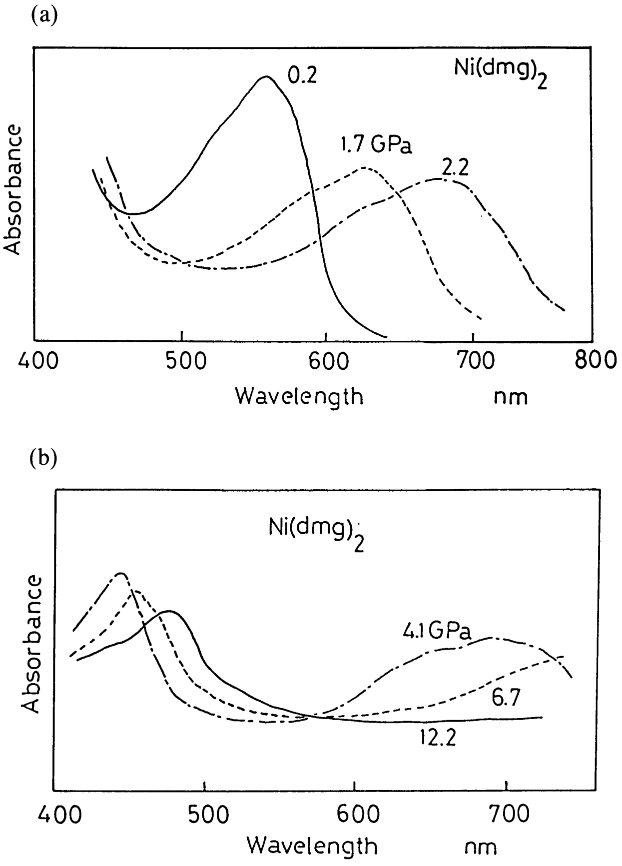
Electronic Spectra. Figure 2 shows the absorption spectra of thin films of $[Ni(dmg)_2]$, $[Ni(niox)_2]$, $[Ni(dpg)_2]$, and $[Ni(bqd)_2]$. The thickness of the films was about 1000 Å. The three characteristic bands in the films were observed over the 200—900 nm range. The 280, 410, and 530 nm bands in the film of $[Ni(dmg)_2]$ correspond to the polarized absorption spectra of the single crystal studied by Ohashi et al.[11] The 280 and 410 nm bands in the film are ascribed to the π–π^*

transition in the ligand and the M–L transition, respectively. The 530 nm band in the film is due to the $3d_{z^2}$–$4p_z$ transition. The polarized reflectance spectra of a single crystal of [Ni(dpg)$_2$] were measured using an optical system comprising a microscope and a monochromator as well as a photodetector at room temperature. Figure 3 shows the polarized reflectance spectra of a single crystal of [Ni(dpg)$_2$]. Since the 430 nm (23300 cm^{-1}) band is polarized perpendicular to the needle axis, the band is assigned to the M–L transition. The 510 nm (19600 cm^{-1}) band is polarized parallel to the needle axis. This band is ascribed to $3d_{z^2}$–$4p_z$ transition. These crystalline spectra correspond to both bands in a film of [Ni(dpg)$_2$]. The spectral features of [Ni(niox)$_2$] are analogous to those of [Ni(dmg)$_2$]. The polarized reflectance spectra of [Ni(bqd)$_2$] have already been measured in the 500—800 nm region.[18] The 750 nm band in a film of [Ni(bqd)$_2$] corresponds to the $3d_{z^2}$–$4p_z$ transition of the crystalline spectra. The d–p band of [Ni(bqd)$_2$] is at a much longer wavelength than that of the other nickel complexes. The 440 nm band of this complex has not yet been identified. Detailed results concerning [Ni(bqd)$_2$] will be reported elsewhere.

The absorption intensity of [Ni(niox)$_2$], [Ni(dmg)$_2$], and [Ni(dpg)$_2$] shows some interesting features: The intensity increases in the order [Ni(niox)$_2$]<[Ni(dmg)$_2$]<[Ni(dpg)$_2$] for the M–L band and, on the contrary, in the order [Ni(dpg)$_2$]<[Ni(dmg)$_2$]<[Ni(niox)$_2$] for the d–p band. The M–L bands of the nickel complexes are located at much longer wavelengths compared with those of the palladium and platinum complexes. The absorption intensity of those bands of the nickel complexes is stronger than that of the palladium and platinum complexes. Thus, the effect of pressure on the M–L bands of the nickel complexes can easily be studied.

The absorption spectra of [Ni(dmg)$_2$], [Ni(niox)$_2$], and [Ni(dpg)$_2$] were measured in the 400—800 nm region at high pressures. Polycrystalline samples were used in this experiment. Figures 4a and 4b show the absorption spectra of [Ni(dmg)$_2$] at high pressures. The d–p band at around 530 nm shifted to longer wavelengths with a pressure increase at the rate of ca. −840 cm^{-1}/GPa in the 0—6 GPa region. This agrees with the result of Drickamer et al.[4,5] The M–L band at around 410 nm showed a red shift at a rate of ca. −330 cm^{-1}/GPa in the same presure region. This is about 1/3 of the pressure shift of the d–p band.

Figure 5 shows the absorption spectra of [Ni(niox)$_2$] at high pressures. The d–p band at around 530 nm shifted to longer wavelengths with increasing pressure at a rate of ca. −810 cm^{-1}/GPa in the 0—6 GPa region. The M–L band at around 410 nm showed red shift at a rate of ca. −320 cm^{-1}/GPa. This is about 1/3 of pressure shift of the d–p band. The rate of the pressure shift of [Ni(niox)$_2$] is slightly smaller than that of [Ni(dmg)$_2$]. The absorption intensity of the M–L band of [Ni(niox)$_2$] rapidly decreased above 10 GPa. The M–L band of the complex was hardly observed at 14 GPa.



Figs. 4a and 4b. Absorption spectra of [Ni(dmg)$_2$] at high pressures.

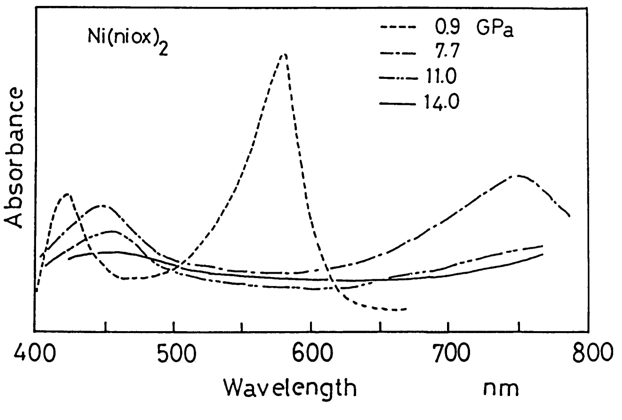


Fig. 5. Absorption spectra of [Ni(niox)$_2$] at high pressures.

Figure 6 depicts the absorption spectra of [Ni(dpg)$_2$] at high pressures. The d–p band at around 510 nm shifted remarkably to longer wavelengths at rates of ca. −1300 cm^{-1}/GPa. The absorption peak were not located in the visible region above 6 GPa. The rate of the red shift of the M–L band is ca. −620 cm^{-1}/GPa. This is about 1/2 of pressure shift of the d–p band. Both bands of [Ni(dpg)$_2$] showed a marked red shift

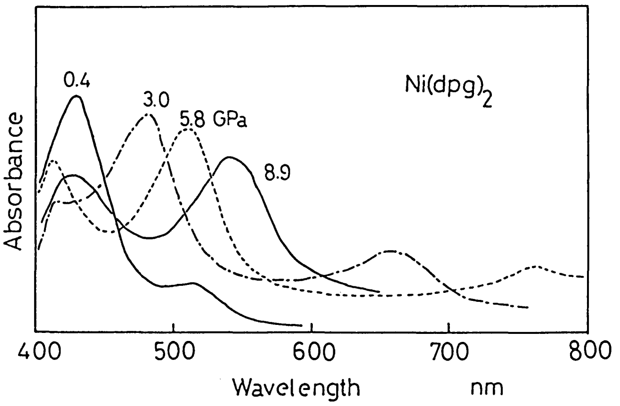


Fig. 6. Absorption spectra of [Ni(dpg)$_2$] at high pressures.

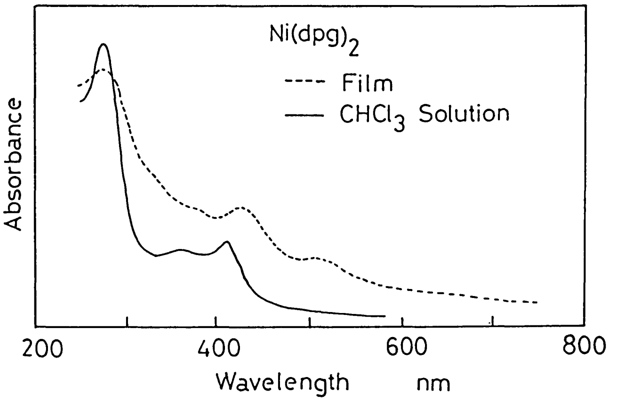


Fig. 7. Absorption spectra in the CHCl$_3$ solution and in the film of [Ni(dpg)$_2$].

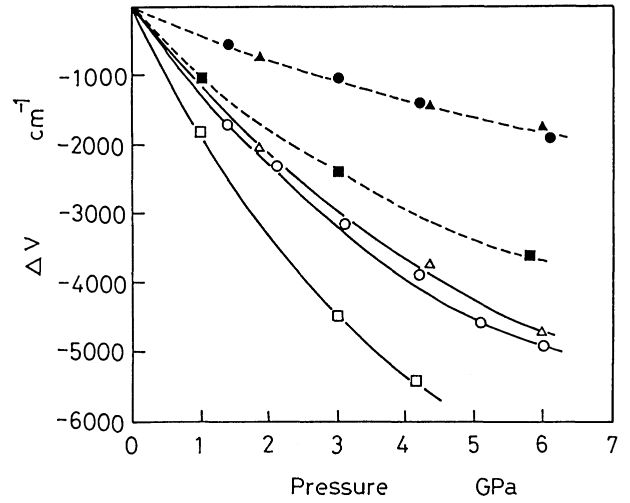


Fig. 8. Pressure shifts of the d–p and M–L bands of the three nickel complexes. The energies of absorption peaks at atmospheric pressure are given in Table 1.

[Ni(dmg)$_2$]: ○, d–p band; ●, M–L band.
[Ni(niox)$_2$]: △, d–p band; ▲, M–L band.
[Ni(dpg)$_2$]: □, d–p band; ■, M–L band.

Table 1. Physical Properties of Bis(1,2-dionedioximato)nickel(II) Complexes

	[Ni(dmg)$_2$]	[Ni(niox)$_2$]	[Ni(dpg)$_2$]
Ni–Ni distance/Å	3.255[a]	3.237[b]	3.52[c]
Absorption peaks			
$\nu_{\text{M-L}}$(max.)/cm^{-1}	24400	24400	23300
d$\nu_{\text{M-L}}$/dP/cm^{-1}/GPa	−330	−320	−620
$\nu_{\text{d-p}}$(max.)/cm^{-1}	18900	18200	19600
d$\nu_{\text{d-p}}$/dP/cm^{-1}/GPa	−840	−810	−1300
Resistivity at 23 GPa/Ω cm	50	7×10^5	2×10^3

a) Ref. 9. b) *J. Chem. Soc.*, **1958**, 3579. c) Ref. 20.

compared with those of [Ni(dmg)$_2$] and [Ni(niox)$_2$]. Above 3 GPa a new absorption band appeared at around 410 nm. This new band was not observed for [Ni(dmg)$_2$] and [Ni(niox)$_2$] at high pressures. Figure 7 shows the absorption spectra in a chloroform solution and in a film of [Ni(dpg)$_2$]. The absorption bands of [Ni(dpg)$_2$] in the solution were observed at around 360 and 410 nm. Both bands correspond to those found at around 328 and 377 nm for [Ni(dmg)$_2$]. The 328 and 377 bands are assigned to the M–L bands of B_{3u} and B_{2u} symmetry, respectively.[11] The 360 and 410 nm bands of [Ni(dpg)$_2$] may be ascribed to the M–L bands of B_{3u} and B_{2u} symmetry, respectively. As is shown in Fig. 7, the 370 and 410 nm bands in the film correspond to both bands in the solution. The 370 nm band of [Ni(dpg)$_2$], that may correspond to the M–L band of B_{3u} symmetry, shifted to longer wavelength with increasing pressure, and appeared in the visible region above 3 GPa.

Recently, the effect of pressure on the absorption spectra of [Pt(dpg)$_2$] has been studied.[15] The rates of the red shift with pressure were ca. −1900 cm^{-1}/GPa for M-L band and ca. −3000 cm^{-1}/GPa for d-p band. These values are much larger than those of [Ni(dpg)$_2$]. The new band observed for [Ni(dpg)$_2$] was not found for [Pt(dpg)$_2$] at high pressure.

Figure 8 shows the pressure shifts of the M–L and d–p bands of three nickel complexes. The mean rates of the red shifts of these bands are summarized in Table 1. There are several characteristic spectral features: (1) The excitations shift remarkably to lower energies with increasing pressure. (2) The rates of the peak shifts for the d–p and M–L bands increase in the order [Ni(niox)$_2$] $<$[Ni(dmg)$_2$]$<$[Ni(dpg)$_2$]. (3) The peak shifts of the M–L bands are much smaller than those of the d–p bands.

We have studied the crystal structure of [Pt(dmg)$_2$] using X-ray diffraction at high pressure.[19] [Pt(dmg)$_2$] crystallizes in the space group *Ibam* and lattice constants of a_0=16.774, b_0=10.579, c_0=6.518 Å, Z=4. The ratios of lattice constants at high pressures to those at atmospheric pressure (a/a_0, b/b_0, c/c_0) decreases rapidly with pressure. The lattice constant shrinks about 9% for the c-axis (needle axis) and about 4.5% for the a- and b-axes up to 4 GPa. The lattice constants of nickel complexes have not yet been investigated at high pressure. [Ni(dmg)$_2$] and [Pt(dmg)$_2$] are isostructural. [Ni(dmg)$_2$] has lattice constants of a_0=16.68, b_0=10.44, c_0=6.49 Å, Z=4. These almost agree with the lattice constants of [Pt(dmg)$_2$]. Thus, the lattice constants of [Ni(dmg)$_2$] at high pressures would be expected to agree with the results of [Pt(dmg)$_2$]. The c-axis of [Ni(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 the Ni–Ni bonds. The d_{z^2} and p_z orbitals extend in the direction of the c-axis. Thus, the d–p band shows a marked red shift with decreasing Ni–Ni distance. Polarization of the transition for the M–L band is perpendicular to the c-axis. The M–L band is the transition from the d_{yz} and d_{zx} (dπ) orbitals in the central metal to the π^* orbital in the ligand. It is reasonable that the pressure shift of the M–L band is much lower than that of the d–p band because the compressibility of the a- and b-axes is about half that compared with that of the c-axis. The absorption bands of [Ni(dpg)$_2$] showed the largest red shift with increasing pressure in the three nickel complexes. The crystal packing of [Ni(dpg)$_2$] is very loose because of a bulky phenyl group. [Ni(dpg)$_2$] has the largest Ni–Ni distance (3.52 Å) of the three nickel complexes.[20] Thus, the optical properties of [Ni(dpg)$_2$] are very sensitive to pressure.

New pressure-induced absorption bands have been found for [Pt(dmg)$_2$], [Pt(bqd)$_2$] and [Pt(niox)$_2$] at room temperature.[3,7] These bands have been assigned to an intramolecular d–d transition. The anomalous absorption spectra were not observed for the nickel complexes at high pressure.

Pressure Indicator Bis(1,2-dionedioximato)metal(II) [Ni, Pd, Pt] complexes are chemically stable, and have various fine colors at atmospheric pressure. Since the absorption bands of these complexes shift to longer wavelengths with pressure, the colors change rapidly with increasing pressure. For example, the color of [Pd(niox)$_2$] turns from yellow to orange, and then to successive colors in the visible spectrum with increasing pressure.[21] We recently observed the pressure-sensitive absorption spectra of [Pt(dpg)$_2$]; the color of the complex turns from red-brow (atmospheric pressure) to brown (0.27 GPa), to green (0.69 GPa), to yellow green (1.24 GPa) and to yellow (1.92 GPa) with increasing pressure.[15] If the relationship between the color and the pressure is studied in detail, a semiquantitative value of pressure could be obtained from a visual observation of the color change with pressure.[22] This can be utilized as an indicator of pressure by a colorimetric method similar to pH testing paper. The absorption bands of [Ni(dmg)$_2$] shift remarkably to longer wavelengths with pressure. Thus, the color of the complex turned from red (atmospheric pressure) to green (1.7 GPa) and to yellow green (5 GPa). Nickel complexes are also available as an indicator of pressure.

Electrical Resistivity. Bis(1,2-dionedioximato)nickel(II) complexes crystallize in columnar structures. These columns are formed by square planar complex molecules with Ni–Ni bond in the direction of the stacks. The overlap of the d_{z^2} orbitals can, thus, produce a band that is completely filled and separated from the next empty band formed by the p_z orbitals due to a large gap. The nickel complexes are insulators with a resistivity of 10^{15} Ω cm at atmospheric pressure.[13] Figure 9 shows the electrical resistivity of [Ni(dmg)$_2$], [Ni(niox)$_2$] and [Ni(dpg)$_2$] at high pressures. Polycrystalline pellets of the complexes were used in this experiment. The resistivity decreased rapidly with increasing pressure over the 0—30 GPa region. An anomaly in the resistivity-pressure curve of [Ni(dpg)$_2$] was observed at around 20 GPa. This unusual behavior may be due to a pressure-induced phase transition. The lowest resistivities of the three nickel complexes were about 50 Ω cm for [Ni(dmg)$_2$], 7×10^5 Ω cm for [Ni(niox)$_2$], and 2×10^3 Ω cm for [Ni(dpg)$_2$] at around 23 GPa. Tkacz and Drickamer have reported the pressure shift of the d–p band of [Ni(dmg)$_2$] up to 32 GPa.[5] The shift tends to become level above 20 GPa. A similar tendency was also found in the resistivity-pressure curve of [Ni(dmg)$_2$]. The resistivity of [Ni(dmg)$_2$] at high pressure may mainly be interpreted in terms of a decrease in the band gap between filled $3d_{z^2}$ valence and $4p_z$ conduction bands with shrinking Ni–Ni distance. The lowest resistivity of [Ni(niox)$_2$] is 10^4 higher than that of [Ni(dmg)$_2$]. As is shown in Table 1, the pressure shift of the d–p band of [Ni(niox)$_2$] is slightly smaller than that of [Ni(dmg)$_2$]. However, the marked differences in the resistivities for

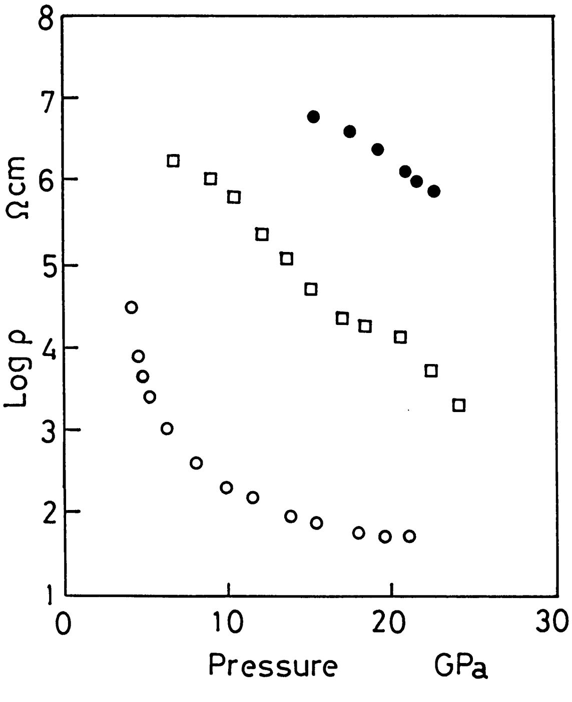


Fig. 9. Electrical resistivity of the three nickel complexes at high pressures.
○, [Ni(dmg)$_2$]; ●, [Ni(niox)$_2$]; □, [Ni(dpg)$_2$].

both complexes can not be explained in terms of a pressure shift of the d–p band.

The intramolecular and intermolecular backbondings play an important role in achieving the low resistivity of the complexes.[23,24] Since the d electrons of the metal penetrate into electron-poor ligands through intramolecular backbonding, the coulomb repulsion between the d electrons on the metal is reduced. The absorption intensity of the M–L band of [Ni(niox)$_2$] is weaker than that of [Ni(dmg)$_2$] and [Ni(dpg)$_2$] at atmospheric pressure. As is shown in Fig. 5, the intensity of this band rapidly decreased above 10 GPa. Thus, the backbonding effect must be weak at higher pressures. The high resistivity of [Ni(niox)$_2$] at high pressure may be closely related to a decrease in the intramolecular backbonding. [Ni(dpg)$_2$] has a longer Ni–Ni distance of 3.52 Å in the linear chain. However, the resistivity of [Ni(dpg)$_2$] is lower than that of [Ni(niox)$_2$] at various pressures. The absorption intensity of the M–L band of [Ni(dpg)$_2$] is strong at atmospheric pressure. The energy of the M–L band is the lowest, and the pressure shift of this band is largest of the three nickel complexes. As is shown in Fig. 6 the new band, which has been assigned to M–L band of B_{3u} symmetry, is found above 3 GPa. Both M–L bands of B_{3u} and B_{2u} symmetry appeared in the visible region at high pressure. These results suggest that the backbonding effect for [Ni(dpg)$_2$] becomes stronger at higher pressures.

The electrical resistivity of [Pt(bqd)$_2$], [Pt(dmg)$_2$], and [Pt(niox)$_2$] drastically decreases with increasing pressure, and reaches a resistivity minimum at higher pressures. Further, pressure-induced insulator-to-metal-to-semiconductor transitions are observed for [Pt(bqd)$_2$] and [Pt(dmg)$_2$] at around the pressure at which the resistivity minimum was observed.[7] No anomalous electrical behavior was found for bis(1,2-dionedioximato)nickel(II) complexes, at least up to 23 GPa.

References

1) Y. Hara, I. Shirotani, and A. Onodera, *Solid State Commun.*, **19**, 171 (1976).

2) I. Shirotani, A. Onodera, and Y. Hara, *J. Solid State Chem.*, **40**, 180 (1981).

3) I. Shirotani and T. Suzuki, *Solid State Commun.*, **59**, 533 (1986).

4) J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960).

5) M. Takacz and H. G. Drickamer, *J. Chem. Phys.*, **85**, 1184 (1986).

6) I. Shirotani, M. Konno, and Y. Taniguchi, *Synth. Met.*, **29**, F123 (1989).

7) I. Shirotani, A. Kawamura, K. Suzuki, W. Utsumi, and and T. Yagi, *Bull. Chem. Soc. Jpn.*, **64**, 1607 (1991).

8) E. Frasson, C. Panattoni, and R. Zannetti, *Acta Crystallogr.*, **12**, 1027 (1959).

9) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).

10) B. C. Anex and F. K. Krist, *J. Am. Chem. Soc.*, **89**, 6114 (1967).

11) Y. Ohashi, I. Hanazaki, and S. Nagakura, *Inorg. Chem.*, **9**, 2551 (1970).

12) M. Cowie, A. Glazes, G. W. Grynkewish, D. M. Kalina, M. C. McClure, R. P. Scainge, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 2921 (1979).

13) L. Atkinson, P. Day, and R. J. P. Williams, *Nature*, **218**, 668 (1968).

14) I. Shirotani, N. Minobe, Y. Ohotsuki, H. Yamochi, and G. Saito, *Chem. Phys. Lett.*, **147**, 231 (1988).

15) I. Shirotani, Y. Inagaki, W. Utsumi, and T. Yagi, *J. Mater. Chem.* **1**, 1041 (1991).

16) J. D. Banett, S. Block, and G. J. Piermarini, *Rev. Sci. Instrum.*, **44**, 1 (1973).

17) N. Kawai, M. Togaya, and A. Onodera, *Proc. Jpn. Acad.*, **49**, 623 (1973).

18) J. M. Brill, M. M. Bélombé and M. Novotny, *J. Chem. Phys.*, **68**, 585 (1978).

19) M. Konno, T. Okamoto, and I. Shirotani, *Acta Crystallogr., Sect. B*, **45**, 142 (1988).

20) A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, **89**. 5507 (1967).

21) I. Shirotani, *Platinum Met. Rev.*, **31**, 20 (1987).

22) I. Shirotani, *Gendai Kagaku (in Japanese)*, **191**, No 2, 30 (1987).

23) M. M. Bélombé, *J. Solid State Chem.*, **22**, 151 (1977).

24) J. S. Miller, *Inorg. Chem.*, **15**, 2357 (1976); *ibid.*, **16**, 957 (1977).