Electrical Conduction of Bis(1,2-diondioximato)metals(II) and Their Partially Oxidized Complexes at High Pressures

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The resistivity of one-dimensional d^8-metal complexes with various kinds of 1,2-diondioxime(dimethylglyoxime, nioxime, and diphenylglyoxime) ligands has been measured at high pressures. The resistivity of $M(dmg)_2$ and $M(niox)_2$ decreased with increasing pressure. The resistivity of $M(dmg)_2$ is much lower than that of $M(niox)_2$ at high pressure, though M–M distances and optical energy gaps in both salts are almost the same at atmospheric pressure. An anomalous low resistivity has been observed in $Pt(dmg)_2$ at about 40 kbar. The electrical resistivity of $M(niox)_2$ and $M(dmg)_2$, oxidized by oxidizing agents, decreased with increasing pressure. The resistivity of partially oxidized Pt complexes is significantly higher than that of the parent compounds at high pressure. On the contrary, partially oxidized Ni and Pd complexes are more conductive than unoxidized compounds at high pressures. The electrocal resistivity of unoxidized and partially oxidized Pt complexes increased with increasing pressure at higher pressures. The resistivity minimum at high pressure has been observed only in Pt complexes. The infrared spectra of the d^8-metal complexes and their partially oxidized complexes have been investigated. The frequency of the C=N stretching vibration in $M(dmg)_2$ and $M(niox)_2$ salts increases in the order Ni > Pd > Pt; on the other hand, the frequency of $M(niox)_2 X_n$ increases in the order Ni < Pd < Pt. The frequency of the C=N stretching vibration is closely related to the effect of metal–ligand π^* back bonding in d^8-metal complexes. Some anomalies in the resistance–pressure curve have been found in $Ni(dpg)_2$, $Ni(dpg)_2I$, $Ni(dpg)_2I_{0.5}$, and $Ni(dpg)_2I_{0.14}$. The anomalies are explained by new pressure-induced phase transitions.

Introduction

The electrical and optical properties of one-dimensional d^8-metal complexes with various kinds of 1,2-diondioxime ligands have been studied (1–4). These materials have been investigated for the purpose of developing new one-dimensional conductors and Little's hypothetical high-temperature excitonic superconductor (5). The resistivity of d^8-metal complexes with dioxime ligands is very high at atmospheric pressure (6). However, Belombe has reported that the resistivity of bis(1,2-ben-

zoquinonedioximato)platinum(II) is very low, about 10^3 ohm cm (7). This has the shortest Pt–Pt distance (3.18 Å) in known d^8-bis(1,2-diondioximato)Pt(II) complexes. The electrical and optical properties of the d^8-complexes are sensitive to decrease of the metal–metal distance. The resistivities decrease abruptly with increasing pressure (2), and the absorption bands show a large red shift with pressure (2, 8). Especially, in the case of bis(dimethylglyoximato)Pt(II), unusually low resistivity has been observed at about 40 kbar. This arises from tightening of the metal–metal

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bond with decreasing interchain metal–metal (M–M) distance.

The d^8-complexes with dioxime are partially oxidized by electron acceptors such as halogen, so new mixed-valence compounds are formed (1, 4, 9–11). The M–M distance in the complexes becomes shorter than that in the corresponding unoxidized complexes. However, the conductivity of the mixed valence compounds is surprisingly low compared with that of K_2 Pt(CN)$_4$Br$_{0.3}$3H$_2$O. Recently, Cowie et al. found that a single crystal of bis(diphenylglyoximato) Ni (II) oxidized by iodine is considerably conductive (12).

We have studied the infrared spectra and the effect of pressure on the electrical resistivity in unoxidized and partially oxidized d^8-metal complexes with several 1,2-diondioximes(dimethylglyoxime, nioxime, diphenylglyoxime), M(ligand)$_2X_n$ (M: Ni, Pd, Pt, X: oxidizing agent). This paper reports some findings on the electrical and optical properties in these materials.

Experimental

Pt(ligand)$_2$ and Pd(ligand)$_2$ were prepared from an aqueous solution of K_2MCl_4 and an alcoholic solution of 1,2-diondioxime. The 1,2-diondioximes used in this experiment are dimethylglyoxime(dmg), diphenylglyoxime(dpg), and 1,2-cyclohexanediondioxime[nioxime (niox)]. The d^8-complexes were easily oxidized by oxidizing agents (electron acceptors) in hot o-dichlorobenzene, so the mixed valence compounds, M(ligand)$_2X_n$, were formed. These were obtained as fine black particles. Ni(dpg)$_2$I$_n$ was prepared as described in the literature (12).

Resistivity measurements at high pressure were undertaken using a split-sphere apparatus (13). Electrical resistivity of the polycrystalline pellets of the compounds was measured as a function of pressure at room temperature. Infrared spectra were

obtained with a Hitachi 260-10 IR spectrophotometer.

Results and Discussion

Ni(dmg)$_2$ (14), Pd(dmg)$_2$ (15), and Pt(dmg)$_2$ (16) crystallize in the space group Ibam and are nearly isostructural. The molecules are planar. The Pd(dmg)$_2$ and Pt(dmg)$_2$ molecules appear to be less symmetrical than the Ni(dmg)$_2$ molecule. M(niox)$_2$ molecules are not planar because of the cyclohexane ring. The M–M distances between metallic atoms of overlying molecules in M(dmg)$_2$ and M(niox)$_2$ are summarized in Table I.

Figure 1 shows the electrical resistivity of Ni(dmg)$_2$, Pd(dmg)$_2$, Ni(niox)$_2$, and Pd(niox)$_2$ at high pressures. The resistivities of the dioxime salts are very high, above 10^{10} ohm cm at atmospheric pressure. The resistivities decreased continu-
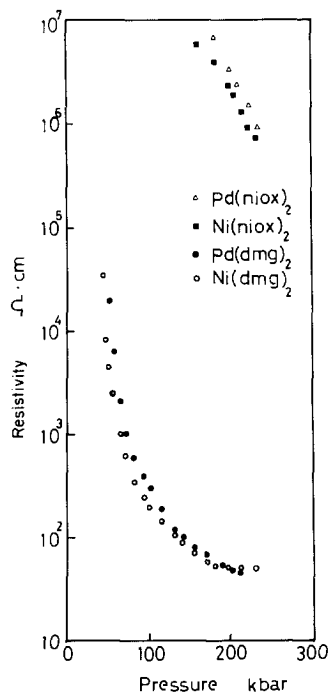

FIG. 1. The electrical resistivity of Ni(dmg)$_2$, Pd(dmg)$_2$, Ni(niox)$_2$, and Pd(niox)$_2$ at high pressures.

TABLE I

PHYSICAL PROPERTIES OF d^8-METAL COMPLEXES

Salt	M–M distance (Å)	Absorption peak (cm^{-1})	Rate of pressure shift (cm^{-1}/kbar)	Frequency of C≡N stretching vibration (cm^{-1})	Lowest resistivity at high pressures (ohm cm)
Ni(dmg)$_2$	3.245(15)[a]	18950(8)	−92.3(8)	1565	5 × 10
	3.233(17)				(230 kbar)
Pd(dmg)$_2$	3.253(17)	22170(8)	−89.2(8)	1540	5 × 10
	3.26(15)			1500	(230 kbar)
Pt(dmg)$_2$	3.23(16)	16280(8)	−117.0(8)	1536	1 × 10^{-1}
				1482	(40 kbar)
Ni(niox)$_2$	3.237(17)	18210(8)	−100.0(8)	1560	7 × 10^5
					(230 kbar)
Pd(niox)$_2$	3.250(17)	21500(8)	−81.4(8)	1535	1 × 10^6
				1493	(230 kbar)
Pt(niox)$_2$		14300(2)	−110.0(2)	1535	2.3
				1490	(100 kbar)

[a] Reference number in parentheses.

ously with increasing pressure up to 300 kbar. The resistivities of specimens could hardly be measured below about 100 kbar because the resistance of the pressure medium, pyrophyllite, is from 10^7 to 10^8 ohms. Figure 2 depicts the resistivity-pressure curve for Pt(dmg)$_2$ and Pt(niox)$_2$. The resistivities decrease drastically with increasing pressure in the low pressure region. The lowest resistivities of Pt(dmg)$_2$ and Pt(niox)$_2$ are 0.1 ohm cm at about 40 kbar and 2.3 ohm cm at about 100 kbar, respectively. Above these pressures, the resistivities increase with increasing pressure. A resistivity minimum at high pressure has been observed only in the Pt complexes.

The energies of the absorption bands in M(dmg)$_2$ salts that are assigned to the optical $nd \to (n + 1)p$ interband transition are slightly higher than those in M(niox)$_2$ salts. The absorption bands show the very large red shifts with increasing pressure. The rate of pressure shifts is given in Table I. Judging from the pressure shifts, the optical energy gaps of M(dmg)$_2$ and M(niox)$_2$ salts are almost the same at high pressures. However, it should be noted that M(dmg)$_2$ salts are more conductive than M(niox)$_2$ salts. The infrared spectra of M(niox)$_2$ are more complexes than those of M(dmg)$_2$ (17, 18). This is due to the existence of the cyclohexane ring which can hardly be planar in M(niox)$_2$. The infrared spectra in Pt(dmg)$_2$
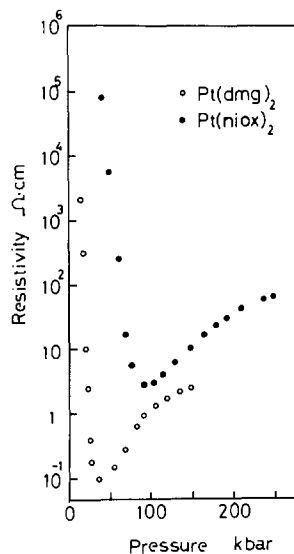

FIG. 2. The electrical resistivity of Pt(dmg)$_2$ and Pt(niox)$_2$ at high pressures.

and Pt(niox)$_2$ are illustrated in Fig. 7. The infrared spectrum of Pt(dmg)$_2$ is not sensitive to pressure (20). On the other hand, remarkable change upon compression has been observed in the infrared spectrum of Pt(niox)$_2$ (21). The M-M distance in Pt(niox)$_2$ can scarcely be shortened at very high pressure for a marked variation of molecular vibrations with pressure. Thus, M(niox)$_2$ salts becomes less conductive at very high pressures.

The resistivity of the Pt complexes is much lower than that of the Pd and Ni complexes at high pressures. This comes mainly from the larger spatial extension of the 5d orbital in Pt complexes compared with 3d or 4d orbitals. The absorption bands in Pt(dmg)$_2$ and Pt(niox)$_2$ are observed at 15.1 × 10^3 and 14.3 × 10^3 cm^{-1}, respectively, both of which are due to $5d_{z^2}$ – $6p_z$ interband electronic transition. The magnitude of the red shift with pressure is −8500 cm^{-1} is about 65 kbar for Pt(dmg)$_2$ (8) and −4400 cm^{-1} at 40 kbar for Pt(niox)$_2$ (2). This shows that the band gap between the filled $5d_{z^2}$ valence and the empty $6p_z$ conduction band remarkably decreased with decreasing interchain metal–metal separation. The absorption edge of thin film of Pt(dmg)$_2$ is located at about 12.8 × 10^3 cm^{-1}. Thus, the optical energy gap at the pressure which shows the resistivity minimum is about 0.5 eV.

On the other hand, the thermal energy gap obtained from the temperature dependence of the resistivity is about 0.01 eV at the same pressure. The $5d_{z^2}$ band of the Pt(dmg)$_2$ is filled at atmospheric pressure. However, anomalously low resistivity and activation energy have been observed at high pressures. The compaction conductivity of microcrystals of one-dimensional conductors indicates an exponentially activated behavior because of interparticle contact resistance (22). Considering this point, the Pt(dmg)$_2$ may be "metallic" at high pressure.

Miller has proposed an intermolecular back-bonding model in order to rationalize the structure of the highly conducting one-dimensional oxalatoplatinates (23). The intermolecular back-bonding may be important for Pt(dmg)$_2$ at high pressure. In the case of Pt(dmg)$_2$, the intermolecular distance of 3.03 Å between the oxygen atoms bound by a hydrogen bond is significantly longer than the one in Ni(dmg)$_2$ and Pd(dmg)$_2$. The O–H–O bond in the Pt(dmg)$_2$ molecule is very weak. The interatomic distance between platinum in Pt(dmg)$_2$ molecule and the oxygen of an adjacent Pt(dmg)$_2$ molecule within a column must considerably decrease at high pressure. An electron seems to be transfered from the Pt metal of a Pt(dmg)$_2$ molecule to the oxygen of adjacent Pt(dmg)$_2$ molecule with a weak hydrogen bond at high pressure. The $5d_{z^2}$ band may change from a filled band to a partial empty band as a result of intermolecular charge transfer at high pressure.

Endres et al. have reported that most of the d^8-bis(1,2-diondioximato)M(II) complexes could be partially oxidized by iodine and crystallized in columnar stacks with linear triiodide chains. The M-M distances in the mixed valence copounds are shorter than those in the corresponding unoxidized forms. However, the conductivity of the salts is surprisingly low (1).

Pt(dmg)$_2$ and Pt(niox)$_2$ are very highly conductive at high pressure because of the decrease of M-M distances. It is expected that the conductivity of the complexes may be enhanced by partial oxidation of the metal ion at atmospheric pressure.

Figure 3 shows the electrical resistivity of Pt(dmg)$_2$I$_{0.2}$ at high pressure. The resistivity was above 10^8 ohm cm at atmospheric pressure, and decreased with increasing pressure up to 200 kbar. It is interesting to note that the partially oxidized compound is less conductive than the unoxidized one, Pt(dmg)$_2$ at high pressures.
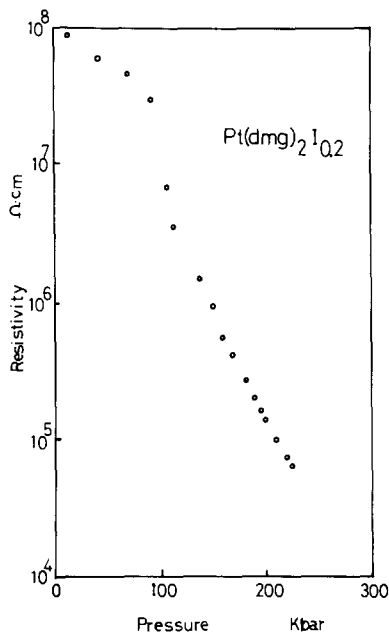
FIG. 3. The electrical resistivity of Pt(dmg)$_2$I$_{0.2}$ at high pressures.

Figure 4 exhibits the effect of pressure on the resistivity of Pt(niox)$_2$I$_n$ (n: 0.2, 0.7, 1.5). The electrical resistivity changed continuously with increasing pressure up to 300 kbar. The position of resistivity minimum moved to higher pressure from 94 kbar in Pt(niox)$_2$ to 122 kbar in Pt(niox)$_2$I$_{0.2}$, to 218 kbar in Pt(niox)$_2$I$_{0.7}$, to 230 kbar in Pt(niox)$_2$I$_{1.5}$. The lowest resistivity in three iodine complexes was about 20 ohm cm for Pt(niox)$_2$I$_{0.7}$ at high pressures, which, however, was higher than the resistivity of the unoxidized salt, Pt(niox)$_2$.

The electrical resistivities of Pd(niox)$_2$I and Ni(niox)$_2$I$_{0.5}$ at high pressure are shown in Figs. 5a and b. The behavior of the resistivity–pressure curve was very similar to that of Pt(niox)$_2$I$_n$. The resistivity of partially oxidized compounds is much lower than that of unoxidized compounds.

Pt(niox)$_2$ is easily oxidized by organic oxidizing agents such as quinone(Q), chloroanil(CA), and bromoanil(BA). The new compounds were very stable and were ob-

tained as fine black particles. Figure 6 depicts the electrical resistivity of Pt (niox)$_2$Q$_n$, Pt(niox)$_2$CA$_n$, and Pt(niox)$_2$BA$_n$ ($n \approx 1$) at high pressure. Their resistivities decreased with increasing pressure up to about 200 kbar. A resistivity minimum was also observed in these salts. The electrical behavior of the salts with pressure was remarkably different at very high pressure. The order of decreasing resistivity is from Pt(niox)$_2$Q$_n$ to Pt(niox)$_2$CA$_n$ to Pt (niox)$_2$BA$_n$. The lowest resistivity of Pt(niox)$_2$ oxidized by organic oxidizing agents is about one magnitude larger than that in Pt(niox)$_2$I$_n$ at high pressures. The lowest resistivities of M(niox)$_2$X$_n$ are summarized in Table II.

Figure 7 shows the infrared spectra of Pt(niox)$_2$, Pt(niox)$_2$I$_{1.5}$ Pt(niox)$_2$Q$_n$, and Pt(dmg)$_2$. The C=N stretching modes are located at 1536 and 1482 cm^{-1} for Pt(dmg)$_2$, 1535 and 1490 cm^{-1} for Pt(niox)$_2$. The C=N stretching vibration in the Pd complexes slightly shifts toward higher frequency. Ni(dmg)$_2$ and Ni(niox)$_2$ have a single C=N stretching mode. As is shown in Table I, the frequencies of C=N stretching vibrations in M(dmg)$_2$ and M(niox)$_2$ complexes
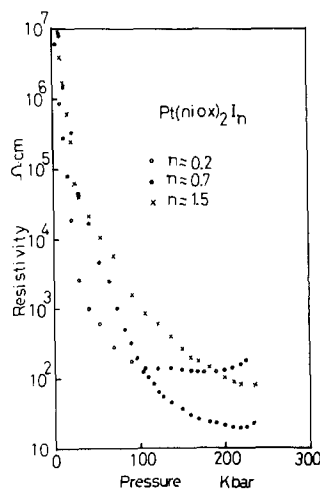

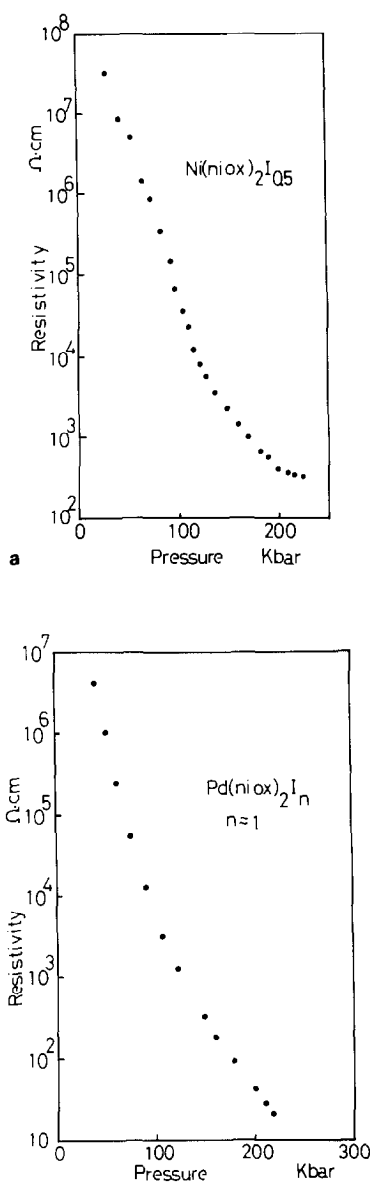FIG. 4. The effect of pressure on the resistivity of Pt(niox)$_2$I$_n$ (n: 0.2, 0.7, 1.5).

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FIG. 5. (a) The effect of pressure on the resistivity of Ni(niox)₂I₀.₅. (b) The effect of pressure on the resistivity of Pd(niox)₂Iₙ ($n \approx 1$).

FIG. 6. The effect of pressure on the resistivity of Pt(niox)₂Qₙ, Pt(niox)₂CAₙ, and Pt(niox)₂BAₙ ($n \approx 1$).

back bonding in $M(\text{dmg})_2$ increases in the order Ni < Pd < Pt from the shift of the C=N frequency (*18*). A similar trend was also found in $M(\text{niox})_2$ salts.

The C=N stretching modes are located at 1589 cm⁻¹ for Pt(niox)₂I₁.₅, 1596 cm⁻¹ for Pt(niox)₂Q. The frequencies shift significantly toward higher energy compared with the unoxidized compound, Pt(niox)₂. Similar results are obtained in

decrease toward the bottom of the Periodic Table. The frequency of the C=N stretching vibration is closely related to the effect of metal–ligand π^* back-bonding in d^8-metal complexes. Burger *et al.* have reported that the effect of metal–ligand π^*
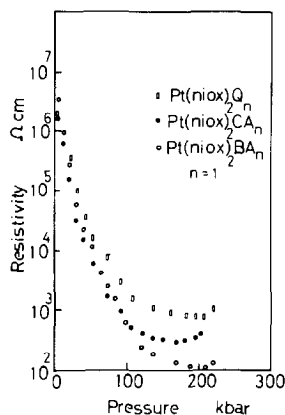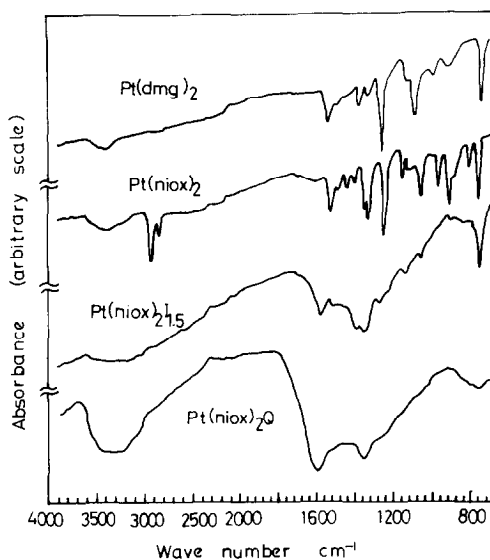

FIG. 7. The infrared spectra of Pt(dmg)₂, Pt(niox)₂, Pt(niox)₂I₁.₅, Pt(niox)₂Qₙ ($n \approx 1$) at room temperature.

partially oxidized $Ni(niox)_2$ and $Pt(niox)_2$. It should be noted that the frequency of the C$=$N stretching vibration in $M(niox)_2X_n$ increases in the order Ni < Pd < Pt. In the case of mixed-valence compounds, the Pt complexes show the lowest metal–ligand π^* back-bonding. Ferraro et al. (24) have reported that the C$\equiv$N stretching vibration in tetracyanoplatinates is sensitive to the degree of oxidation of the platinum, and shifts toward higher frequency as the oxidation state for platinum increases. The trend is explained in term of a decrease in platinum–CN π^* back-bonding.

A number of square planar d^8–Pt complexes at room temperature show a resistivity minimum at high pressures (2, 25–27). The resistivity minimum may be closely related to the metal–ligand π^* back bonding (20, 28). The resistivity minimum in $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ and $Rb_2Pt(CN)_4 Br_{0.2} \cdot 3H_2O$ has been found at room temperature and at about 25 kbar. We have found that the resistivity minimum in the tetracyanoplatinates was not observed at liquid nitrogen temperature, and suggested
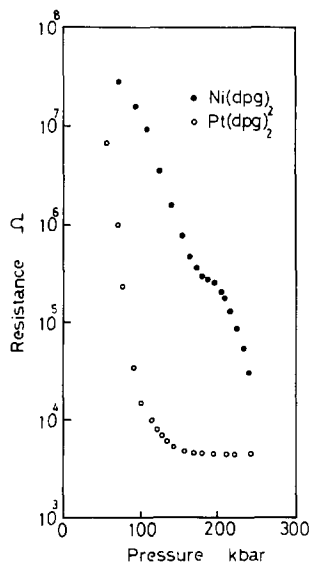

FIG. 8. The pressure dependence of the electrical resistance in $Pt(dpg)_2$ and $Ni(dpg)_2$.

that the resistivity minimum of the compounds observed at room temperature may arise mainly from the dehydration of crystal water (27).

The metal–ligand π^* back-bonding in $Pt(niox)_2X_n$ decreases much more than that in $Pt(niox)_2$. If the resistivity minimum at high pressure depends mainly on π^* back-bonding, it would be expected that the position of the resistivity minimum in $Pt(niox)_2X_n$ would shift to lower pressure compared with $Pt(niox)_2$. However, as is given in Table II, the resistivity minimum in $Pt(niox)_2I_n$ shifts to higher pressure. The results suggest that the effect of π^* back-bonding is not always important for a resistivity minimum in the complexes.

Figure 8 exhibits the electrical resistance of $Pt(dpg)_2$ and $Ni(dpg)_2$ as a function of pressure. The resistance of $Pt(dpg)_2$ leveled off above 250 kbar. On the other hand, an anomaly in the resistance in $Ni(dpg)_2$ appeared around 200 kbar. This unusual behavior may be due to a pressure-induced phase transition.

Oxidation of $Ni(dpg)_2$ with I_2 results in

TABLE II

LOWEST RESISTIVITY OF d^8-METAL COMPLEXES AT HIGH PRESSURES

Salt	ρ_{min} (ohm cm)	ρ_{min} (kbar)
$Pt(niox)_2$	3	94
$Pt(niox)_2I_{0.2}$	8 $\times$ 10	122
$Pt(niox)_2I_{0.7}$	2 $\times$ 10	218
$Pt(niox)_2I_{1.5}$	1.5 $\times$ 10^2	230
$Pt(niox)_2Q_n$ ($n \approx 1$)	8 $\times$ 10^2	204
$Pt(niox)_2CA_n$ ($n \approx 1$)	3 $\times$ 10^2	169
$Pt(niox)_2BA_n$ ($n \approx 1$)	1 $\times$ 10^2	204
$Pt(niox)_2TCNQ_n$ ($n \approx 0.5$)	2 $\times$ 10^3	115
$Ni(niox)_2$	7 $\times$ 10^5	230
$Ni(niox)_2I_{0.5}$	3 $\times$ 10^2	226
$Pd(niox)_2$	1 $\times$ 10^6	230
$Pd(niox)_2I_n$ ($n \approx 1$)	3 $\times$ 10	236
$Pt(dmg)_2$	1 $\times$ 10^{-1}	40
$Pt(dmg)_2I_{0.2}$	6 $\times$ 10^4	230
$Ni(dpg)_2$	2 $\times$ 10^3	230
$Ni(dpg)_2I_{0.5}$	2 $\times$ 10^3	40

near 150 kbar for $Ni(dpg)_2I$. The resistivity in $Ni(dpg)_2I_{0.5}$ decreased abruptly with increasing pressure in the low pressure region. Resistivity maxima appeared around 75 and 200 kbar. Similar resistivity anomalies were also observed in $Ni(dpg)_2I_{0.14}$ at high pressures.

Quasi one-dimensional TCNQ complexes with several phenyl groups such as $[(C_6H_5)_3PCH_3]$- and $[(C_6H_5)_3AsCH_3]TCNQ_2$ have anomalies in their electrical and magnetic properties at high pressures (29, 30). The anomalous behavior has been explained by occurrence of a new phase at high pressures. The crystal packing of the salts is very loose for the existence of bulky phenyl groups. Thus, phase transitions are easily induced at high pressures.

Several anomalies in the resistivity at high pressure were found in $Ni(dpg)_2I_n$. We suggest these are due to the existence of bulky phenyl groups.

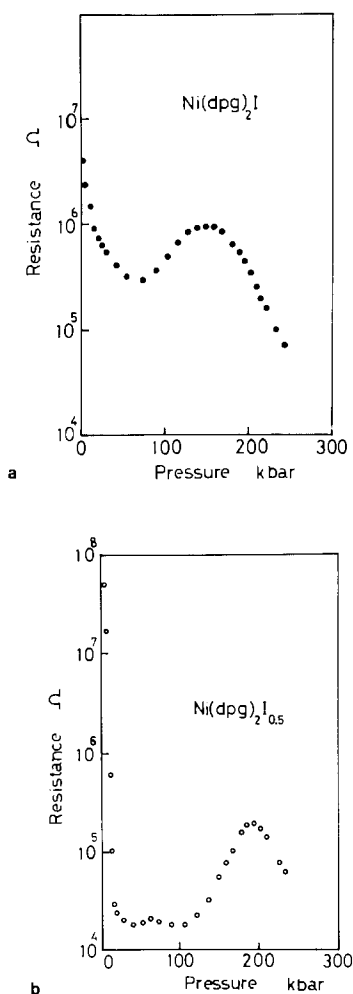FIG. 9. (a) The effect of pressure on the resistance of $Ni(dpg)_2I$. (b) The effect of pressure on the resistance of $Ni(dpg)_2I_{0.5}$.

formation of complexes of $Ni(dpg)_2I_n$. The Ni–Ni distances in partially oxidized compounds become much shorter than that in the parent compound. A crystal structure of $Ni(dgp)_2I$ has been determined in detail (12). The $Ni(dpg)_2$ unit is staggered by 90° with respect to its nearest neighbor along the stacking axis. The iodine atoms stack along the c-axis. The resistance–pressure curve in a compacted specimen of $Ni(dpg)_2I$ and $Ni(dpg)_2I_{0.5}$ is illustrated in Figs. 9a and b. A resistivity maximum was observed

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