

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 $M(\text{dmg})_2$ and $M(\text{niox})_2$ decreased with increasing pressure. The resistivity of $M(\text{dmg})_2$ is much lower than that of $M(\text{niox})_2$ 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 $\text{Pt}(\text{dmg})_2$ at about 40 kbar. The electrical resistivity of $M(\text{niox})_2$ and $M(\text{dmg})_2$, 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 $\text{C}=\text{N}$ stretching vibration in $M(\text{dmg})_2$ and $M(\text{niox})_2$ salts increases in the order $\text{Ni} > \text{Pd} > \text{Pt}$; on the other hand, the frequency of $M(\text{niox})_2X_n$ increases in the order $\text{Ni} < \text{Pd} < \text{Pt}$. The frequency of the $\text{C}=\text{N}$ 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 $\text{Ni}(\text{dpg})_2$, $\text{Ni}(\text{dpg})_2\text{I}$, $\text{Ni}(\text{dpg})_2\text{I}_{0.5}$, and $\text{Ni}(\text{dpg})_2\text{I}_{0.14}$. 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

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 $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$. Recently, Cowie *et al.* found that a single crystal of bis(diphenylglyoximate) 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), $M(\text{ligand})_2X_n$ (M : Ni, Pd, Pt, X : oxidizing agent). This paper reports some findings on the electrical and optical properties in these materials.

Experimental

$Pt(\text{ligand})_2$ and $Pd(\text{ligand})_2$ 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(dm g), diphenylglyoxime(d p g), 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, $M(\text{ligand})_2X_n$, were formed. These were obtained as fine black particles. $Ni(dpg)_2I_n$ 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

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

Figure 1 shows the electrical resistivity of $Ni(dm\text{g})_2$, $Pd(dm\text{g})_2$, $Ni(niox)_2$, 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-

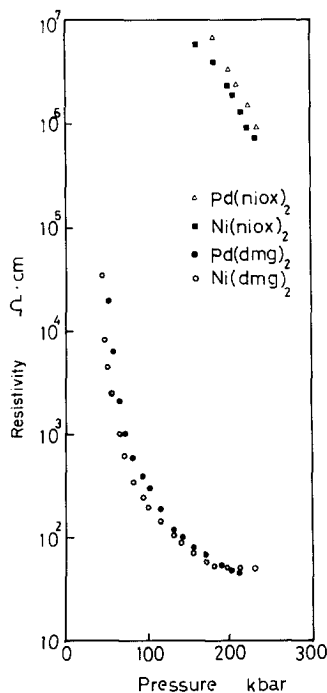


FIG. 1. The electrical resistivity of $Ni(dm\text{g})_2$, $Pd(dm\text{g})_2$, $Ni(niox)_2$, and $Pd(niox)_2$ at high pressures.

TABLE I
 PHYSICAL PROPERTIES OF d^8 -METAL COMPLEXES

Salt	$M-M$ distance (Å)	Absorption peak (cm^{-1})	Rate of pressure shift ($\text{cm}^{-1}/\text{kbar}$)	Frequency of C=N stretching vibration (cm^{-1})	Lowest resistivity at high pressures (ohm cm)
Ni(dmg) ₂	3.245(15) ^a 3.233(17)	18950(8)	-92.3(8)	1565	5×10 (230 kbar)
Pd(dmg) ₂	3.253(17) 3.26(15)	22170(8)	-89.2(8)	1540 1500	5×10 (230 kbar)
Pt(dmg) ₂	3.23(16)	16280(8)	-117.0(8)	1536 1482	1×10^{-1} (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 1493	1×10^6 (230 kbar)
Pt(niox) ₂		14300(2)	-110.0(2)	1535 1490	2.3 (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 $M(\text{dmg})_2$ salts that are assigned to the optical $nd \rightarrow (n+1)p$ interband transition are slightly higher than those in $M(\text{niox})_2$ 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 $M(\text{dmg})_2$ and $M(\text{niox})_2$ salts are almost the same at high pressures. However, it should be noted that $M(\text{dmg})_2$ salts

are more conductive than $M(\text{niox})_2$ salts. The infrared spectra of $M(\text{niox})_2$ are more complexes than those of $M(\text{dmg})_2$ (17, 18). This is due to the existence of the cyclohexane ring which can hardly be planar in $M(\text{niox})_2$. The infrared spectra in Pt(dmg)₂

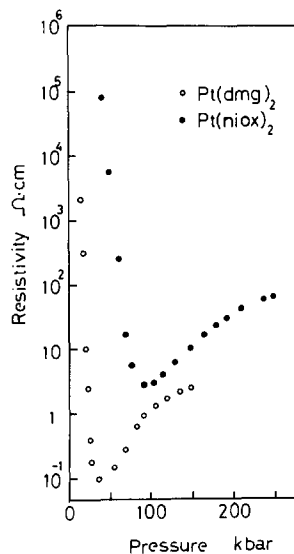


FIG. 2. The electrical resistivity of Pt(dmg)₂ and Pt(niox)₂ at high pressures.

and $\text{Pt}(\text{niox})_2$ are illustrated in Fig. 7. The infrared spectrum of $\text{Pt}(\text{dmg})_2$ is not sensitive to pressure (20). On the other hand, remarkable change upon compression has been observed in the infrared spectrum of $\text{Pt}(\text{niox})_2$ (21). The $M-M$ distance in $\text{Pt}(\text{niox})_2$ can scarcely be shortened at very high pressure for a marked variation of molecular vibrations with pressure. Thus, $M(\text{niox})_2$ 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 $\text{Pt}(\text{dmg})_2$ and $\text{Pt}(\text{niox})_2$ are observed at 15.1×10^3 and $14.3 \times 10^3 \text{ cm}^{-1}$, 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 $\text{Pt}(\text{dmg})_2$ (8) and -4400 cm^{-1} at 40 kbar for $\text{Pt}(\text{niox})_2$ (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 $\text{Pt}(\text{dmg})_2$ is located at about $12.8 \times 10^3 \text{ cm}^{-1}$. 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 $\text{Pt}(\text{dmg})_2$ 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 $\text{Pt}(\text{dmg})_2$ 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 $\text{Pt}(\text{dmg})_2$ at high pressure. In the case of $\text{Pt}(\text{dmg})_2$, the intermolecular distance of $3.03 \text{ \AA}$ between the oxygen atoms bound by a hydrogen bond is significantly longer than the one in $\text{Ni}(\text{dmg})_2$ and $\text{Pd}(\text{dmg})_2$. The O-H-O bond in the $\text{Pt}(\text{dmg})_2$ molecule is very weak. The interatomic distance between platinum in $\text{Pt}(\text{dmg})_2$ molecule and the oxygen of an adjacent $\text{Pt}(\text{dmg})_2$ molecule within a column must considerably decrease at high pressure. An electron seems to be transferred from the Pt metal of a $\text{Pt}(\text{dmg})_2$ molecule to the oxygen of adjacent $\text{Pt}(\text{dmg})_2$ 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) $M(\text{II})$ 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).

$\text{Pt}(\text{dmg})_2$ and $\text{Pt}(\text{niox})_2$ 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 $\text{Pt}(\text{dmg})_2\text{I}_{0.2}$ 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, $\text{Pt}(\text{dmg})_2$ at high pressures.

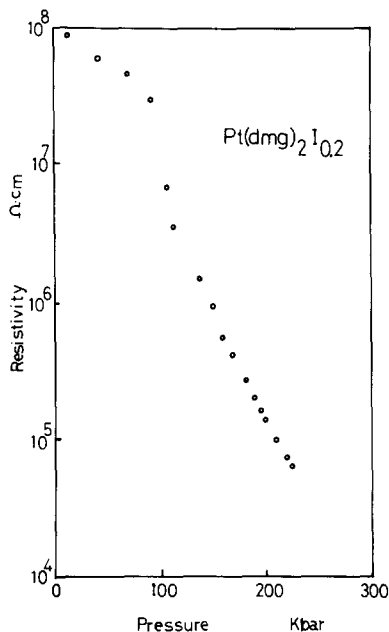


FIG. 3. The electrical resistivity of $\text{Pt}(\text{dmgi})_2\text{I}_{0.2}$ at high pressures.

Figure 4 exhibits the effect of pressure on the resistivity of $\text{Pt}(\text{niox})_2\text{I}_n$ (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 $\text{Pt}(\text{niox})_2$ to 122 kbar in $\text{Pt}(\text{niox})_2\text{I}_{0.2}$, to 218 kbar in $\text{Pt}(\text{niox})_2\text{I}_{0.7}$, to 230 kbar in $\text{Pt}(\text{niox})_2\text{I}_{1.5}$. The lowest resistivity in three iodine complexes was about 20 ohm cm for $\text{Pt}(\text{niox})_2\text{I}_{0.7}$ at high pressures, which, however, was higher than the resistivity of the unoxidized salt, $\text{Pt}(\text{niox})_2$.

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

$\text{Pt}(\text{niox})_2$ 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 $\text{Pt}(\text{niox})_2\text{Q}_n$, $\text{Pt}(\text{niox})_2\text{CA}_n$, and $\text{Pt}(\text{niox})_2\text{BA}_n$ ($n \approx 1$) 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 $\text{Pt}(\text{niox})_2\text{Q}_n$ to $\text{Pt}(\text{niox})_2\text{CA}_n$ to $\text{Pt}(\text{niox})_2\text{BA}_n$. The lowest resistivity of $\text{Pt}(\text{niox})_2$ oxidized by organic oxidizing agents is about one magnitude larger than that in $\text{Pt}(\text{niox})_2\text{I}_n$ at high pressures. The lowest resistivities of $M(\text{niox})_2\text{X}_n$ are summarized in Table II.

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

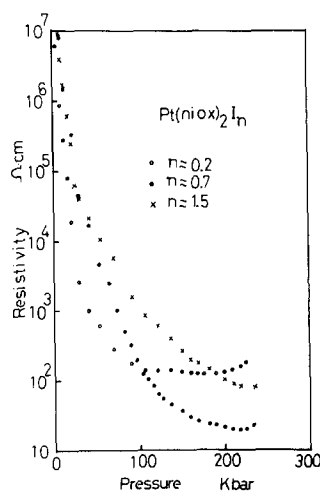


FIG. 4. The effect of pressure on the resistivity of $\text{Pt}(\text{niox})_2\text{I}_n$ (n : 0.2, 0.7, 1.5).

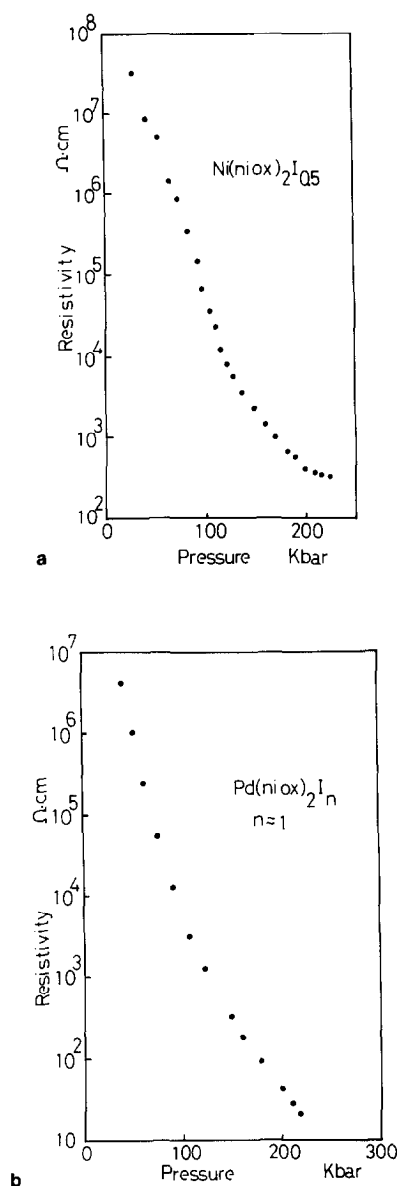


FIG. 5. (a) The effect of pressure on the resistivity of $\text{Ni}(\text{niox})_2\text{I}_{0.5}$. (b) The effect of pressure on the resistivity of $\text{Pd}(\text{niox})_2\text{I}_n$ ($n \approx 1$).

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^*

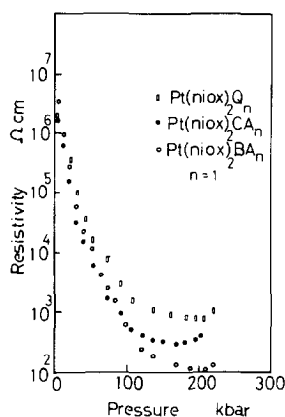


FIG. 6. The effect of pressure on the resistivity of $\text{Pt}(\text{niox})_2\text{Q}_n$, $\text{Pt}(\text{niox})_2\text{CA}_n$, and $\text{Pt}(\text{niox})_2\text{BA}_n$ ($n \approx 1$).

back bonding in $M(\text{dmg})_2$ increases in the order $\text{Ni} < \text{Pd} < \text{Pt}$ 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 $\text{Pt}(\text{niox})_2\text{I}_{1.5}$, 1596 cm^{-1} for $\text{Pt}(\text{niox})_2\text{Q}$. The frequencies shift significantly toward higher energy compared with the unoxidized compound, $\text{Pt}(\text{niox})_2$. Similar results are obtained in

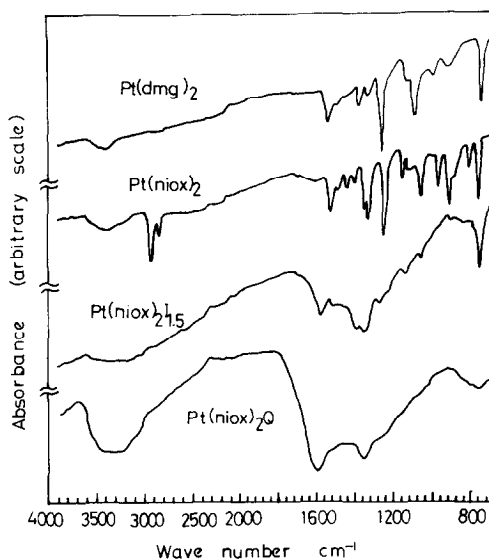


FIG. 7. The infrared spectra of $\text{Pt}(\text{dmg})_2$, $\text{Pt}(\text{niox})_2$, $\text{Pt}(\text{niox})_2\text{I}_{1.5}$, $\text{Pt}(\text{niox})_2\text{Q}_n$ ($n \approx 1$) at room temperature.

partially oxidized $\text{Ni}(\text{niox})_2$ and $\text{Pt}(\text{niox})_2$. It should be noted that the frequency of the $\text{C}\equiv\text{N}$ stretching vibration in $M(\text{niox})_2X_n$ increases in the order $\text{Ni} < \text{Pd} < \text{Pt}$. 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 $\text{C}\equiv\text{N}$ 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 $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ and $\text{Rb}_2\text{Pt}(\text{CN})_4\text{Br}_{0.2} \cdot 3\text{H}_2\text{O}$ 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

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

Salt	$\rho_{\min}$ (ohm cm)	$\rho_{\min}$ (kbar)
$\text{Pt}(\text{niox})_2$	3	94
$\text{Pt}(\text{niox})_2\text{I}_{0.2}$	8×10	122
$\text{Pt}(\text{niox})_2\text{I}_{0.7}$	2×10	218
$\text{Pt}(\text{niox})_2\text{I}_{1.5}$	1.5×10^2	230
$\text{Pt}(\text{niox})_2\text{Q}_n$ ($n \approx 1$)	8×10^2	204
$\text{Pt}(\text{niox})_2\text{CA}_n$ ($n \approx 1$)	3×10^2	169
$\text{Pt}(\text{niox})_2\text{BA}_n$ ($n \approx 1$)	1×10^2	204
$\text{Pt}(\text{niox})_2\text{TCNQ}_n$ ($n \approx 0.5$)	2×10^3	115
$\text{Ni}(\text{niox})_2$	7×10^5	230
$\text{Ni}(\text{niox})_2\text{I}_{0.5}$	3×10^2	226
$\text{Pd}(\text{niox})_2$	1×10^6	230
$\text{Pd}(\text{niox})_2\text{I}_n$ ($n \approx 1$)	3×10	236
$\text{Pt}(\text{dmg})_2$	1×10^{-1}	40
$\text{Pt}(\text{dmg})_2\text{I}_{0.2}$	6×10^4	230
$\text{Ni}(\text{dpg})_2$	2×10^3	230
$\text{Ni}(\text{dpg})_2\text{I}_{0.5}$	2×10^3	40

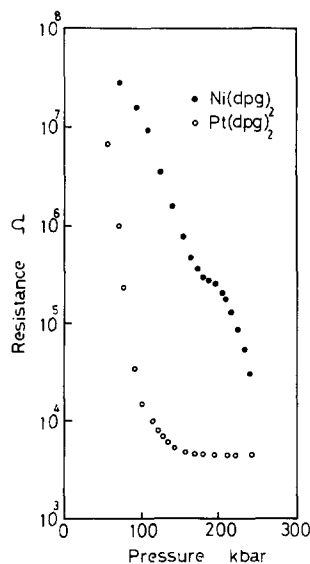


Fig. 8. The pressure dependence of the electrical resistance in $\text{Pt}(\text{dpg})_2$ and $\text{Ni}(\text{dpg})_2$.

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 $\text{Pt}(\text{niox})_2X_n$ decreases much more than that in $\text{Pt}(\text{niox})_2$. 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 $\text{Pt}(\text{niox})_2X_n$ would shift to lower pressure compared with $\text{Pt}(\text{niox})_2$. However, as is given in Table II, the resistivity minimum in $\text{Pt}(\text{niox})_2\text{I}_n$ 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 $\text{Pt}(\text{dpg})_2$ and $\text{Ni}(\text{dpg})_2$ as a function of pressure. The resistance of $\text{Pt}(\text{dpg})_2$ leveled off above 250 kbar. On the other hand, an anomaly in the resistance in $\text{Ni}(\text{dpg})_2$ appeared around 200 kbar. This unusual behavior may be due to a pressure-induced phase transition.

Oxidation of $\text{Ni}(\text{dpg})_2$ with I_2 results in

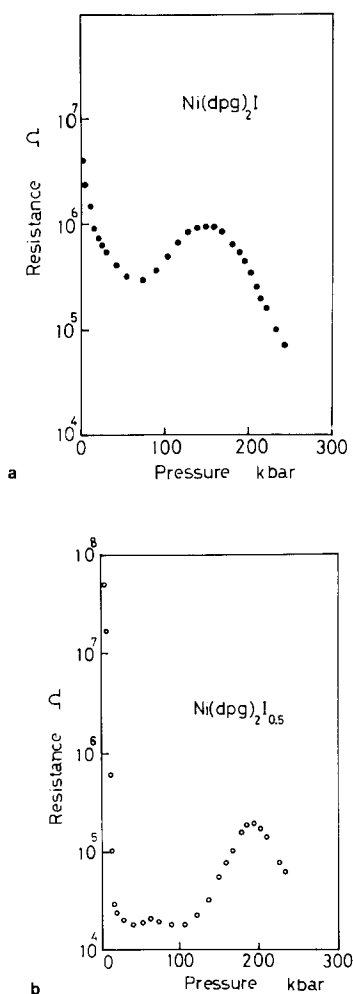


FIG. 9. (a) The effect of pressure on the resistance of $\text{Ni(dpg)}_2\text{I}$. (b) The effect of pressure on the resistance of $\text{Ni(dpg)}_2\text{I}_{0.5}$.

formation of complexes of $\text{Ni(dpg)}_2\text{I}_n$. The Ni–Ni distances in partially oxidized compounds become much shorter than that in the parent compound. A crystal structure of $\text{Ni(dpg)}_2\text{I}$ 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 $\text{Ni(dpg)}_2\text{I}$ and $\text{Ni(dpg)}_2\text{I}_{0.5}$ is illustrated in Figs. 9a and b. A resistivity maximum was observed

near 150 kbar for $\text{Ni(dpg)}_2\text{I}$. The resistivity in $\text{Ni(dpg)}_2\text{I}_{0.5}$ 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 $\text{Ni(dpg)}_2\text{I}_{0.14}$ at high pressures.

Quasi one-dimensional TCNQ complexes with several phenyl groups such as $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]\text{-}$ and $[(\text{C}_6\text{H}_5)_3\text{AsCH}_3]\text{TCNQ}_2$ 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 $\text{Ni(dpg)}_2\text{I}_n$. We suggest these are due to the existence of bulky phenyl groups.

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