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A RESISTANCE MINIMUM AND THE ELECTRONIC STRUCTURES OF SOME ONE-DIMENSIONAL Pt-COMPLEXES AT HIGH PRESSURES

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The effect of pressure has been measured up to 650 kbar on the electrical resistance in six one-dimensional Pt-complexes, including two mixed valence ones. $SrPt(CN)_4 \cdot 2H_2O$, $MgPt(CN)_4 \cdot 7H_2O$ and $BaPt(CN)_4 \cdot 4H_2O$ do not show a resistance minimum, contrary to other d^8-metal complexes, suggesting a considerable contribution of π^* orbitals of CN^- ligands to the conduction.

A LOT OF STUDIES have been carried out for one-dimensional Pt-complexes. The authors found that the electrical resistance for both $MgPt(CN)_4 \cdot 7H_2O$(MgCP)[1] and $Pt(DMG)_2$[2] decreased by a factor of 10^{-5} and 10^{-16} up to 180 kbar. Interrante and Bundy[3,4] investigated the resistance dependence on pressure in $Pt(NH_3)_4PtCl_4$ (MGS), cis-$[Ir(CO)_2(acac)]$ and $K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 2.3H_2O$(KCP). All the d^8-metal complexes except for MgCP which have been studied so far show a resistance minimum at high pressures. Some of them have been known to decrease greatly in the visible absorption energy up to a certain pressure above which it begins to increase.[5]

In this paper, we will present the results of the high pressure electrical resistance experiments for the one-dimensional square-planar Pt-complexes which are listed in Table 1, four Pt(II) complexes; $SrPt(CN)_4 \cdot 2H_2O$, $MgPt(CN)_4 \cdot 7H_2O$, $BaPt(CN)_4 \cdot 4H_2O$, $Pt(NH_3)_4 \cdot PtCl_4$, and two mixed-valence complexes; $K_{1.7}Pt(CN)_4 \cdot 1.8H_2O$ and $K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$. The zero pressure resistivities of the polycrystalline samples are also displayed in Table 1.

The electrical resistance was measured as a function of pressure up to 180 kbar, using a supported-taper piston apparatus[6] and up to 650 kbar, using a split-sphere apparatus.[7] By multiplying the observed resistance by a factor of 10^{-1}, the approximate resistivity under high pressure can be calculated.

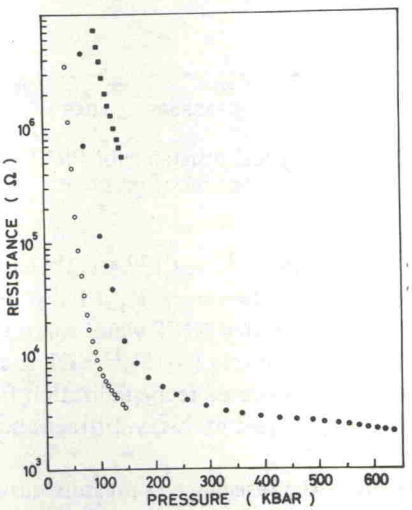

FIG. 1. The electrical resistance of various $Pt(CN)_4^{2-}$ derivatives as a function of pressure: ○, $SrPt(CN)_4 \cdot 2H_2O$; ●, $MgPt(CN)_4 \cdot 7H_2O$; ■, $BaPt(CN)_4 \cdot 4H_2O$.

Table 1. Materials studied

Complex	Pt–Pt distance (Å)	Pressed pellet resistivity (Ω-cm)[a]	Crystal structure
$K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$(KOP)	2.85	(Single crystal) 5.2×10 (Polycrystalline) 2.8×10^2	Triclinic
$K_{1.7}Pt(CN)_4 \cdot 1.8H_2O$($K_{1.7}$CP)	2.96	2.4×10^2	Triclinic
$SrPt(CN)_4 \cdot 2H_2O$(SrCP)	3.09	$> 10^6$	Monoclinic
$MgPt(CN)_4 \cdot 7H_2O$(MgCP)	3.16	$> 10^6$	Tetragonal
$BaPt(CN)_4 \cdot 4H_2O$(BaCP)	3.32	8.8×10^6	Monoclinic
$Pt(NH_3)_4 \cdot PtCl_4$(MGS)	3.23	1.7×10^4	Tetragonal

[a] At 1 atm and at 20°C.

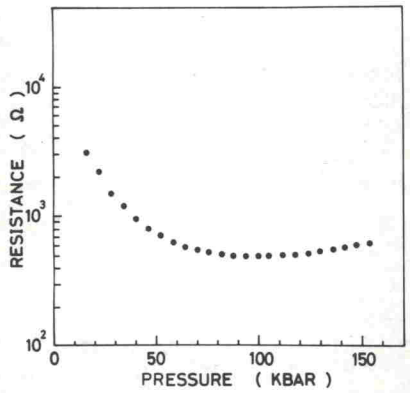

FIG. 2. The electrical resistance of $Pt(NH_3)_4 \cdot PtCl_4$ as a function of pressure.

KOP,[8] SrCP,[9] MgCP,[10] BaCP[10] MGS[10] were prepared as described in the literature. $K_{1.7}$CP was prepared by oxidizing the saturated K_2CP water solution by concentrated nitric acid (N-15).[11] KOP and MGS were purified by the repeated recrystallization from water. $K_{1.7}$CP was identified by X-ray diffraction.[11]

In Fig. 1 the resistance vs pressure curve for the polycrystalline SrCP, MgCP and BaCP are illustrated. The results are reversible and also reproducible. The complexes with the shorter Pt–Pt distance exhibit the better conduction under pressure. It is very interesting that these tetracyano complexes do not show a resistance minimum, since all the one-dimensional d^8-metal complexes studied so far show a resistance minimum. The CN^- ligand is known to be a strong electron-acceptor, using its low lying empty π^* orbitals, i.e. backbonding. There is no doubt that

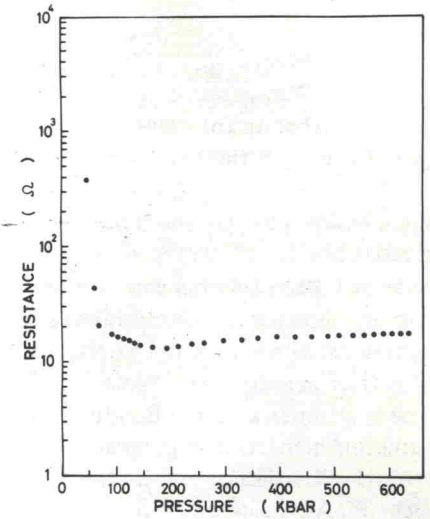

FIG. 3. The electrical resistance of $K_{1.7}Pt(CN)_4 \cdot 1.8H_2O$ as a function of pressure.

CN^- ligands contribute greatly to the electronic structures at high pressures.

Figure 2 exhibits the resistance of MGS as a function of pressure. The results are compatible with those given by Interrante and Bundy.[3] It should be noted that MGS does not have low lying empty π^* orbitals.

The pressure effect on the resistance of $K_{1.7}$CP is displayed in Fig. 3. As $K_{1.7}$CP contains the fractional valency of the Pt (average oxidation number = 2.3) like KCP, about 1/6 of the $5dz^2$ band is empty.[12] The

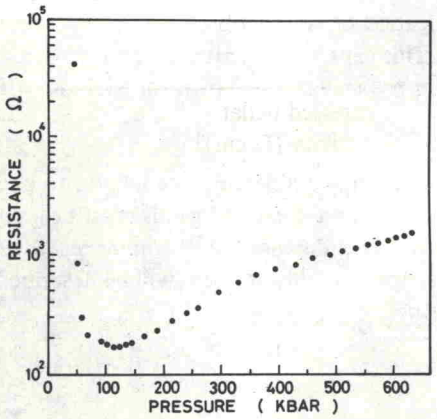

FIG. 4. The electrical resistance of $K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$ as a function of pressure.

electrical behaviors of $K_{1.7}CP$ which is a K^+ deficient complex and of KCP which is a Br^- excessive one are quite different at high pressures; in $K_{1.7}CP$ over ~ 180 kbar the resistance slightly drifts upwards up to 650 kbar, while KCP increases in resistance by a factor of 10^2 over ~ 40 kbar up to ~ 100 kbar.[4] This discrepancy is mainly attributed to the presence of Br^-.

Figure 4 exhibits the pressure effect on the electrical resistance of polycrystalline KOP up to 650 kbar. The average oxidation number of Pt atom is 2.4. A resistance minimum appears at ~ 120 kbar, above which the resistance increases by a factor of 10 up to 650 kbar. It is to be noted again that $C_2O_4^{2-}$ ligand does not have low lying π^* orbitals. The activation energies of a single crystal and a pressed pellet of KOP were measured over the temperature range of 133–463°K. They are 0.062 and 0.097 eV, respectively. However, a resistance jump happens by a factor of 10 at ~ 60°C. At ~ 160°C, KOP begins to decompose. The thermal data, i.e. DTA was also observed. The resistance discontinuity at ~ 60°C well corresponds to the endo to exsothermal change in DTA curve.

In Fig. 5, the pressure vs resistivity curve for the single crystal of KOP is shown. The electron conduction along the needle axis (i.e., the Pt–Pt bonding direction) is larger than that perpendicular to it by a factor of ~ 10^2 at 15 kbar. Above 100 kbar, the anisotropy decreases. This means that the electron hopping from a chain to one of the adjacent chains prevails at high pressures.

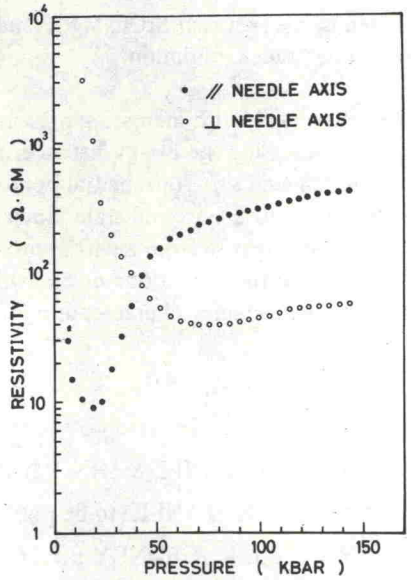

FIG. 5. The electrical resistivity of single crystal $K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$ as a function of pressure.

The values of resistance obtained in Fig. 4 are consistent with the single crystal data. Then it is likely that the decrease in resistance in samples shown in Figs. 1–3 is not just due to better interparticle contact with increasing pressure.

The electrical behavior of the polycrystalline material observed was attributed to the opposing effects on resistance.

The primary interaction between adjacent Pt atoms involves the increase in broadening of $5dz^2$ bands. Then the conduction electron in partially-filled $5dz^2$ bands of $K_{1.7}CP$ and KOP can delocalize further along the chain direction. This is closely reflected by the decrease in the resistance vs pressure curve for above Pt-complexes. As was indicated in the earlier work,[13] the energy difference between $5dz^2$ and $6pz$ orbitals decreases greatly with increasing pressure. Consequently $6pz$ band as well as $5dz^2$ one increases in broadening and overlapping between them. The electrons in the filled $5dz^2$ bands of SrCP, MgCP, BaCP and MGS become easier to be promoted to $6pz$ bands. This causes the resistance to decrease. Empty π^* orbitals of the ligands will greatly aid this tendency in that it decreases the coulombic repulsion between the valence electrons through backbonding. This is

obviously seen in the fact that SrCP, MgCP and BaCP do not show a resistance minimum.

On the other hand, with increasing pressure, therefore with decreasing the Pt–Pt distance, d^2sp^3 octahedral bonding and dsp^2 tetrahedral bonding begins to contribute to the ground state. Such Pt–Pt bond formation which arise from a partial promotion of a $5dz^2$ electron to the vacant $6pz$ orbital will result in a increase in the covalency character and in the relocalization of conduction electrons into new Pt–Pt bonds. This causes an eventual increase in resistance at higher pressures, as is shown for KOP, $K_{1.7}CP$ and MGS.

The results obtained may be helpful to know a part of the conditions that ligands must bear for high conductive one-dimensional Pt-complexes. A further study concerning this problem will be described in the near future.

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