

Purity Effects on the Charge-Transport Properties in One-Dimensional $\text{TPP}[\text{Co}^{\text{III}}(\text{Pc})(\text{CN})_2]_2$ (TPP = Tetraphenylphosphonium and Pc = Phthalocyaninato) Conductors

Satoshi Yamashita, Toshio Naito, and
Tamotsu Inabe*

Department of Chemistry, Graduate School of Science,
Hokkaido University, Sapporo 060-0810

Received December 3, 2008; E-mail: inabe@sci.hokudai.ac.jp

Purity effects on the temperature dependence of electrical resistivity in $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ with a typical one-dimensional metallic electronic system have been examined. In this system, no dependence on the impurity content has been observed, suggesting that the apparent thermally activated behavior is dominated by charge disproportionation.

There are several ground states of one-dimensional (1-D) electronic systems. The Peierls-type insulating state with lattice distortion was once thought to be the most typical ground state. However, charge disproportionation (charge ordering) due to Coulombic interaction without distinct lattice distortion has recently been recognized as a ground state of quarter-filled electronic systems.^{1–7} The phthalocyaninato (Pc) system in this study is also known as a highly 1-D conductor.

There are two types of Pc conductors. One is $[\text{M}(\text{Pc})]\text{X}_y$, $\text{M} = \text{Ni}, \text{Cu}, \text{H}_2$, etc., $\text{X} = \text{I}_3^-, \text{BF}_4^-, \text{PF}_6^-$, etc., and $0.33 < y < 0.5$, in which planar $[\text{M}(\text{Pc})]$ units form a 1-D column with metal-over-metal stacking.⁸ The crystal system is tetragonal, and the 1-D column is surrounded by anions. The electronic interactions between the columns are rather weak, and the electronic system is highly 1-D; the anisotropy of the conduction has been reported to be 500. The conductivity was reported to diminish at low temperature in an early report.⁹ However, in $[\text{Ni}(\text{Pc})]\text{I}$ (the charge is $[\text{Ni}(\text{Pc})]^{1/3+}(\text{I}_3^-)_{1/3}$ and the Pc ring is partially oxidized), metallic conductivity was observed down to 5 K when the samples were prepared from high purity $[\text{Ni}(\text{Pc})]$.¹⁰ The conductivity did not decrease so much at lower temperature; the high conductivity of 10^4 S cm^{-1} was maintained even at 1.85 K. The ground state in $[\text{Ni}(\text{Pc})]\text{I}$ is still puzzling, but this study indicates that the temperature dependence of the conductivity of the Pc system is sensitively affected by impurities.

Another π - π stacking structure is obtained when the axially ligated Pc unit ($[\text{M}(\text{Pc})\text{L}_2]$, $\text{M} = \text{Co}$ and Fe , and $\text{L} = \text{CN}, \text{Cl}$,

and Br) is utilized as a component.⁸ In this case, only the periphery of the Pc ring overlaps with the neighboring ring. A characteristic of this system is that the π - π stacking network varies by the cationic species. When TPP is utilized as the cationic component, a 1-D partially oxidized salt of $\text{TPP}[\text{M}(\text{Pc})\text{L}_2]_2$ is obtained.¹¹ The starting mono-valent anion of $[\text{M}(\text{Pc})\text{L}_2]^-$ is oxidized to $[\text{M}(\text{Pc})\text{L}_2]^{1/2+}$ in this salt. In the crystal, this unit forms a 1-D π - π stacking network. The Pc planes in the neighboring 1-D networks are nearly perpendicular to each other so that there is negligible electronic interaction between them; the anisotropy of the conductivity is about 10^3 for $\text{M} = \text{Co}$ and $\text{L} = \text{CN}$.¹¹ Since the π - π stacking is uniform, this crystal has a metallic 3/4-filled conduction band. However, the conductivity shows thermally activated behavior below room temperature. On the other hand, the thermoelectric power is metallic above 100 K, and the band width estimated from the temperature dependence is about 0.5 eV, which is almost one-half of that in $[\text{Ni}(\text{Pc})]\text{I}$.

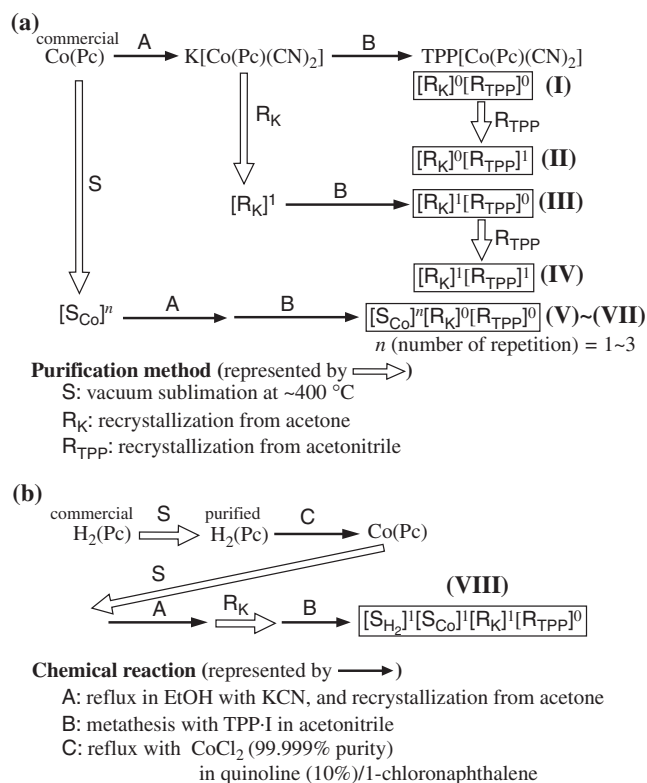
In order to investigate whether this thermally activated behavior is due to lattice distortion, precise X-ray diffraction experiments on $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ were performed at 21 K. Neither super-lattice diffraction nor diffuse streaks were observed. On the other hand, ⁵⁹Co NQR measurements detected an asymmetric signal at low temperature, suggesting charge disproportionation in the crystal.¹²

This interpretation of the ground state is reasonable since the electronic system is highly 1-D. However, since there still remains a possibility that impurities affect the charge transport as found in $[\text{Ni}(\text{Pc})]\text{I}$, it is vital to examine the impurity effects on the transport properties in $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$. In this study, we carried out preparation of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ single crystals from starting material with different impurity levels and measurement of the transport properties.

The purification methods are shown in Scheme 1, and the amount of paramagnetic impurity detected by ESR measurements in the 1:1 salt of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$ (starting material for the electrolysis) for each batch is shown in Table 1. Since Co^{III} in the Pc unit is in the low-spin state, the material should be diamagnetic. Therefore, the paramagnetic species detected in the ESR measurements correspond wholly to impurities; the *g*-factor was always nearly 2.

Purification efficiency in each process is summarized as follows. S_{Co} (sublimation of $[\text{Co}(\text{Pc})]$) reduces the amount of impurities effectively, but repetition (represented by superscript *n*) is not effective. R_{K} (recrystallization of the potassium salt) reduces the amount of impurities, while R_{TPP} increases the impurity level. Since it is not likely that Co^{III} is further oxidized during recrystallization, the π -ligand is thought to be chemically decomposed to form a free radical.

Commercially available $[\text{M}(\text{Pc})]$ s are known to contain impurity metals. In order to exclude the effect of the impurity metals, high purity $[\text{Co}(\text{Pc})]$ was synthesized from purified $[\text{H}_2(\text{Pc})]$ and Co^{2+} with 99.999% purity. $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$ was then synthesized through route (b) in Scheme 1, which was considered to be the route to yield the purest sample. The purity of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$ thus obtained was however, not so much improved. From this result, it is strongly suggested that the paramagnetic species detected by ESR are mainly chemically decomposed ligand. Although some foreign metal ions may be



Scheme 1.

Table 1. Impurity Level in $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$ Purified Following Scheme 1

Sample	Impurity level /ppm	Sample	Impurity level /ppm
I	100	V	30
II	400	VI	60
III	50	VII	40
IV	250	VIII	60

ESR silent, their presence must be much lower in the sample prepared from Co^{2+} with 99.999% purity.

$\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ single crystals were prepared by electrochemical oxidation of the above-mentioned $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]$ samples. The impurity levels may be reduced during electrocrystallization, since the process may eliminate foreign species that occurred in recrystallization. However, the free radical species contained in the present system is rather readily incorporated in the host lattice, since recrystallization of the TPP salt increased the impurity levels. Therefore, the purity of the product must reflect the purity of the starting material as demonstrated in the $[\text{Ni}(\text{Pc})]\text{I}$ system.¹⁰

The temperature dependence of resistivity in some crystals (normalized to the value at room temperature) is shown in Figure 1. The difference between the highest (400 ppm) and lowest (30 ppm) impurity levels is practically negligible. The resistivity of the crystal obtained from the salt prepared from Co^{2+} with 99.999% purity is nearly constant in the high-temperature region, whereas it shows the same increase at low temperature. The room-temperature values are distributed

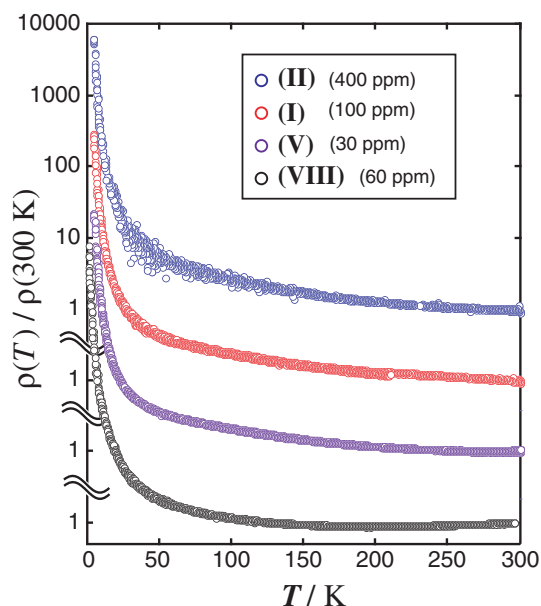


Figure 1. Temperature dependence of the normalized resistivity of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ prepared from starting material with varying purity. The vertical axis for each sample is shifted for clarity.

within $\pm 50\%$ of $10^{-2} \Omega\text{cm}$. The values have no correlation to the impurity level, and disperse even in the same batch.

The results are in contrast to the case of $[\text{Ni}(\text{Pc})]\text{I}$. For $[\text{Ni}(\text{Pc})]\text{I}$, the paramagnetic impurity in starting $[\text{Ni}(\text{Pc})]\text{I}$ seriously affected the temperature dependence of the conductivity, and high conductivity at low temperature was not achieved when the purity level was not high enough.¹⁰ In other words, the apparent thermally activated behavior of the conductivity at low temperature in this 1-D system was dominated by the scattering of carriers by impurities. On the other hand, the 1-D conductor based on the $[\text{Co}(\text{Pc})(\text{CN})_2]$ unit always shows thermally activated behavior of the conductivity at low temperature irrespective of the impurity level. This fact strongly suggests that there is another mechanism that induces charge localization in this system. Even if charge scattering by impurities occurs, the effect could not be seen because another effect that localizes the carriers dominates the charge transport.

Such charge localization may occur by band gap formation at the Fermi level due to $2k_F$ or $4k_F$ lattice distortion. However, this scenario is contradicted by the temperature dependence of the ESR signal, magnetic susceptibility, and low-temperature X-ray diffraction.¹² Consequently, charge disproportionation driven by the electron–electron correlation effect is thought to be most probable.

The temperature dependence of the paramagnetic susceptibility of $\text{TPP}[\text{Co}(\text{Pc})(\text{CN})_2]_2$ prepared from two different starting materials ((V) (30 ppm) and (I) (100 ppm)) is shown in Figure 2. Both samples show similar susceptibility; the main component is temperature independent Pauli-like paramagnetism. It should be noted that the Curie tailing at low temperature is almost 1% (assuming $g = 2$ and $S = 1/2$) in both samples. If this component corresponded to paramagnetic impurities, impurity concentration would be increased by more than 100 times. Since the electrolysis was performed under mild

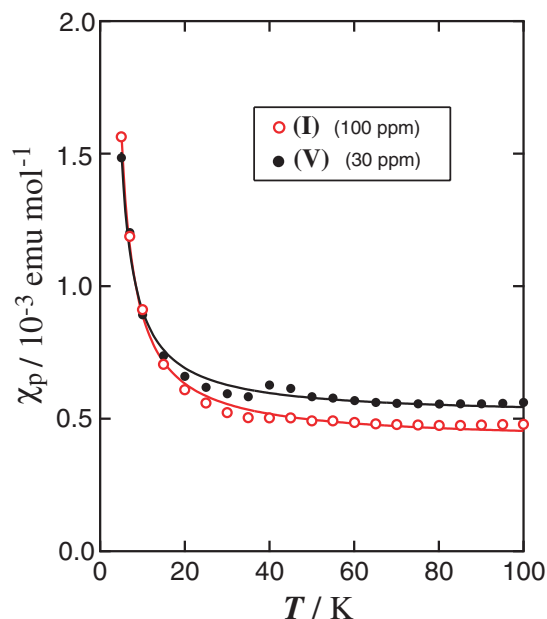


Figure 2. Temperature dependence of the paramagnetic susceptibility of TPP[Co(Pc)(CN)₂]₂. The solid lines correspond to the fitting based on the [Pauli paramagnetism + Curie spin] model. The concentration of the paramagnetic Curie spin ($S = 1/2$) is 0.9% for (V) and is 1.1% for (I).

oxidation conditions, it is not likely that the paramagnetic impurity increases during crystal growth. Therefore, the relatively large Curie component is considered to be due to localized spins originating from charge disproportionation in microscopic domains.

In conclusion, we have studied how purity affects the transport behavior in 1-D metal TPP[Co(Pc)(CN)₂]₂ which shows thermally activated conductivity, and found that paramagnetic impurity has little effect on the transport behavior. These results strongly suggest that the temperature dependence of the conductivity is dominated by charge disproportionation, agreeing with the conclusion drawn from the asymmetric ⁵⁹Co NQR signal in TPP[Co(Pc)(CN)₂]₂.¹²

Experimental

Purification Methods. Commercial [Co(Pc)] was used in the preparation and purification routes in Scheme 1a. Seven kinds of starting materials for electrolysis, TPP[Co(Pc)(CN)₂]₂, were obtained by combining vacuum sublimation and recrystallization.

TPP[Co(Pc)(CN)₂]₂ in the route shown in Scheme 1b was prepared from [Co(Pc)] obtained by the reaction of sublimed commercial [H₂(Pc)] and CoCl₂ with 99.999% purity. Paramagnetic impurity levels were estimated from the ESR signal intensity assuming that the paramagnetic spins obey Curie-like behavior with $S = 1/2$.

Measurements. ESR spectra were obtained with a Bruker EMX spectrometer at room temperature. TPP[Co(Pc)(CN)₂]₂ was used as a standard for spin concentration. Electrical resistivity was measured along the needle axis of the crystal by a standard four-probe method in the temperature range of 5–300 K. Magnetic susceptibility was measured with a Quantum Design MPMS SQUID susceptometer for randomly oriented polycrystalline samples.

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