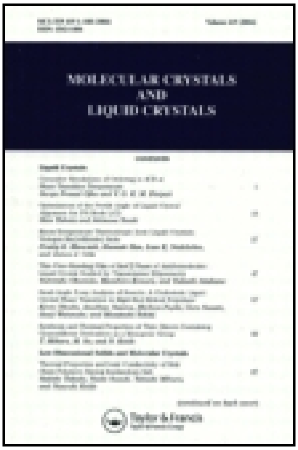

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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One-dimensional π- d system with axially substituted iron(III) phthalocyanine

Masaki Matsuda [a], Toshio Naito [a], Tamotsu Inabe [a], Noriaki Hanasaki [b] & Hiroyuki Tajima [b]

[a] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan

[b] Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba, 277-8581, Japan

To cite this article: Masaki Matsuda, Toshio Naito, Tamotsu Inabe, Noriaki Hanasaki & Hiroyuki Tajima (2003): One-dimensional π- d system with axially substituted iron(III) phthalocyanine, Molecular Crystals and Liquid Crystals, 380:1, 277-282

To link to this article: http://dx.doi.org/10.1080/713738723

Mol. Cryst. Liq. Cryst., Vol. 380, pp. 277-282
Copyright © 2002 Taylor & Francis
1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290102017

ONE-DIMENSIONAL π-*d* SYSTEM WITH AXIALLY SUBSTITUTED IRON(III) PHTHALOCYANINE

Masaki Matsuda, Toshio Naito and Tamotsu Inabe*
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Noriaki Hanasaki and Hiroyuki Tajima
Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

With the axially CN-substituted phthalocyanines, novel one-dimensional conductors, $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$ (M = Co and Fe) have been obtained. Although their crystal structures appear as if they were simple salts, their physical properties show metallic behaviors. These crystals are therefore partially oxidized salts in which part of the cation sites are replaced by CH_3CN. Especially, when M = Fe, the Pc unit has a local magnetic moment and a 1-D π-d system is formed. The existence of the π-d interaction is suggested from the electrical and magnetic measurements.

Keywords: phthalocyanine; one-dimensional conductor; π-*d* system

INTRODUCTION

We have shown that the axially substituted metal phthalocyanine anion, $[M^{III}(Pc)(CN)_2]^-$, is useful to construct novel molecular conductors [1–3]. Furthermore, when the metal ion is Fe^{III}, which is a magnetic species, the system reveals its π-*d* coupled nature [4,5].

Recently, we have found that the electrochemical oxidation of PTMA-$[M^{III}(Pc)(CN)_2]$ (PTMA = phenyltrimethylammonium, M = Co^{III} and Fe^{III}) gives novel one-dimensional conductors. Strangely, in this crystal, both the Pc unit and the cation were found at the $2/m$ symmetry sites in the space group *Pnnm*, appearing as if they were simple salts. However, since they

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This work was partly supported by a Grant-In-Aid for Scientific Research, from the Ministry of Education, Science and Culture, Japanese Government.

*Corresponding author: E-mail: masaki@sci.hokudai.ac.jp are highly conducting, they must be partially oxidized salts, in which the solvents for electrochemical oxidation occupy the cationic sites partially.

CRYSTAL STRUCTURE

The crystal structure of $(PTMA)_x[Fe^{III}(Pc)(CN)_2]\cdot yCH_3CN$, which is completely isostructure with $(PTMA)_x[Co^{III}(Pc)(CN)_2]\cdot yCH_3CN$, is shown in Figure 1 and their crystal data are summarized in Table 1. Orientationally disordered PTMA is also shown in Figure 1. In the crystal, the transla-

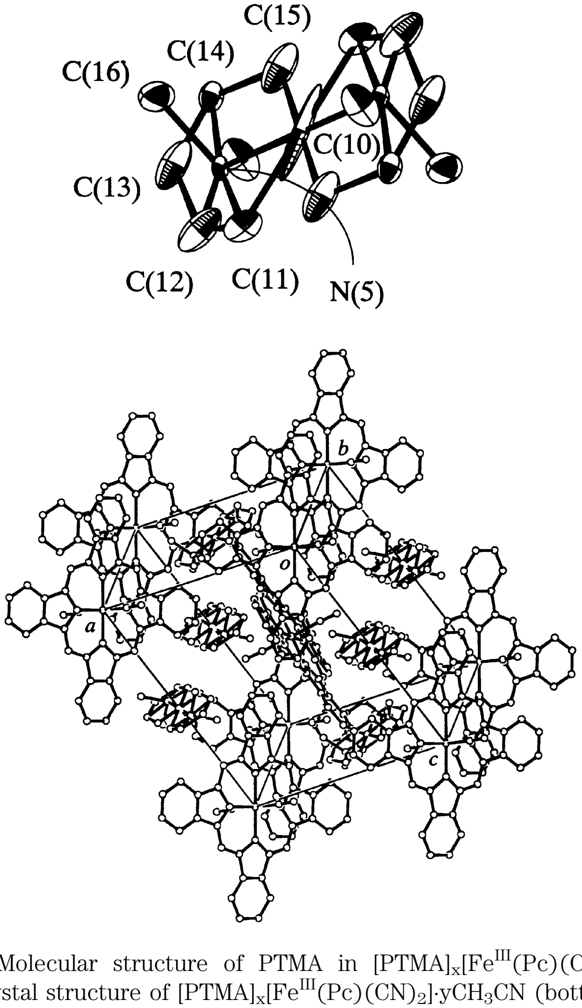

FIGURE 1 Molecular structure of PTMA in $[PTMA]_x[Fe^{III}(Pc)(CN)_2]\cdot yCH_3CN$ (top) and crystal structure of $[PTMA]_x[Fe^{III}(Pc)(CN)_2]\cdot yCH_3CN$ (bottom).

TABLE 1 Crystal Data of $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$

	M = Fe	M = Co
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnnm*	*Pnnm*
a/Å	13.9001(5)	13.8706(6)
b/Å	7.3319(2)	7.3498(3)
c/Å	16.3165(5)	16.2958(7)
V/Å^3	1662.88(8)	1661.3(1)
Z	2	2
R	0.050	0.049

tionally related PC units form a one-dimensional regular chain along the *b*-axis. The interplanar distances between two peripheral benzene rings, with which the Pc units are stacked, are 3.46 Å for both Fe^{III} and Co^{III} salts, and the overlap integral between the Pc rings in a chain is calculated to be 1.0×10^{-2} and 9.4×10^{-3}, for the Fe^{III} salt and the Co^{III} salt, respectively.

Viewing the crystal structure, one may notice that the ratio of PTMA to the Pc unit as 1:1, as if this is the simple salt though the crystal was obtained from the electrochemical oxidation. However, its physical properties are clearly metallic as discussed in Figures 2 and 3. Thus, it is suggested that the title compounds are partially oxidized salts. This suggestion is supported by the fact that the crystal structure of the simple salt, $PTMA[Fe^{III}(Pc)(CN)_2]$, is quite different from that obtained from the electrochemical oxidation.

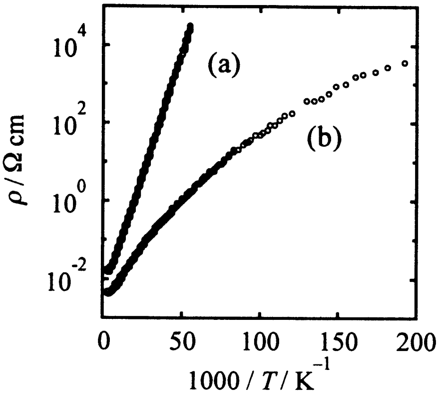

FIGURE 2 Electrical resistivity of $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$; M = Fe (a) and Co (b).

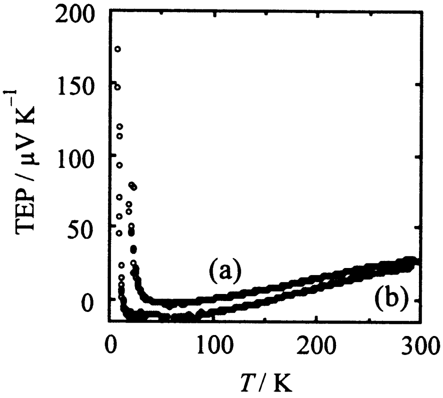

FIGURE 3 Thermoelectric power of $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$; M = Fe (a) and Co (b).

The structure of the crystal obtained by the electrocrystallization was then investigated closely. The X-ray structure analysis suggests that there is the disorder in the cation site, while no disorder in the Pc site. If this compound is a partially oxidized salt, some neutral components should occupy the disordered cation site. Looking over the molecular structure of PTMA with paying attention to the thermal parameters of their components, we found that the thermal parameters for C(10), C(12), C(13), C(15) and C(16) (that is except for C(11), C(14) and N(5)) are considerably large. This indicates that the occupancies for these atoms could be smaller. Furthermore, it can be noticed that the position of C(11) is extraordinarily close to that of C(12), so that C(11) is linearly aligned with N(5) and C(14). These facts suggest that acetonitrile, the solvent, partially occupies the disordered cation site, probably the C(11)-N(5)-C(14) portion.

The bond lengths of Pc were rather insensitive to the charge [2]. Thus, unfortunately, it is not possible to determine the oxidation state (x and y) from the X-ray structure analysis. However, in the IR spectra of $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$, we have observed a peak at 1365 cm^{-1} which can be assigned to the oxidized Pc ligand [6]. This result also supports the suggestion that $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$ is the partially oxidized salt.

ELECTRICAL PROPERTIES

The temperature dependence of the resistivity along the *b*-axis for $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$ (M = Fe^{III} and Co^{III}) is shown in Figure 2. The temperature dependence shows metallic behavior at high temperature, above 270 K and above 230 K for the Fe^{III} and Co^{III} salts, respectively. With lowering the temperature, they show semiconducting behavior. Since the apparent activation energy is larger for the Fe^{III} salt than that for the Co^{III} salt, the difference in the resistivity becomes larger at lower temperature.

Figure 3 represents the temperature dependence of the thermoelectric power (TEP) for $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$. The positive values are consistent with the carrier being a hole generated by oxidation of the Pc π-electrons. The thermoelectric power is linearly correlated to the temperature in a wide temperature range (>20 K for the Co^{III} salt and >40 K for the Fe^{III} salt), suggesting the metallic nature of these salts. From the TEP and overlap integral data, we have attempted to estimate the x value. Assuming the band width is proportional to the overlap integral, the one-dimensional tight-binding band structure model gives x value to be 0.46 with comparing the slopes of the linear portions of the TPP salts.

The inconsistency between the thermoelectric power and conductivity might appear owing to the highly one-dimensional character and the narrow band width ($\sim$0.5 eV); about 50% of the typical metallic $[M(Pc)]_yX$ conductors.

MAGNETIC PROPERTIES

Figure 4 shows the temperature dependence of the magnetic susceptibility for $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$ ($M = Fe^{III}$ and Co^{III}) with x and y are assigned to be 0.5 and 1, respectively, for simplicity. For $(PTMA)_x$-

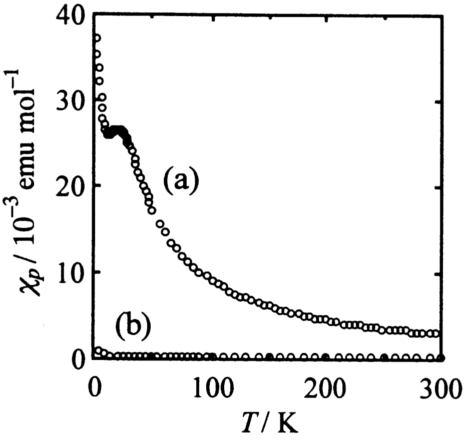

FIGURE 4 Magnetic susceptibility of $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$; M = Fe (a) and M = Co (b).

$[Co^{III}(Pc)(CN)_2]\cdot yCH_3CN$, almost temperature independent Pauli-like susceptibility is observed, while for $(PTMA)_x[Fe^{III}(Pc)(CN)_2]\cdot yCH_3CN$, Curie-like paramagnetism is observed at high temperature. Especially for the Fe^{III} salt, an anomaly at around 20 K, suggesting the existence of the antiferromagnetic interaction, is apparent. This behavior quite resembles that of the TPP salts, which are also the highly one-dimensional conductors [4]. Since the distance between the Fe^{III} atoms is large (>7 Å), the antiferromagnetic interaction between the Fe^{III} atoms must be mediated by the itinerant π-electrons. This means that there is certainly the π-d interaction in this system.

In summary, we have obtained novel one-dimensional conductors, $(PTMA)_x[M^{III}(Pc)(CN)_2]\cdot yCH_3CN$ (M = Fe and Co), in which partially oxidized Pc units form a regular chain along the b-axis. Their electrical resistivity and magnetic susceptibility are quite different depending on whether a metal ion has a magnetic moment or not. For the Fe^{III} salt, the existence of the π-d interaction is suggested, and we have recently observed the giant negative magnetoresistance below 40 K in the preliminary measurements.

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