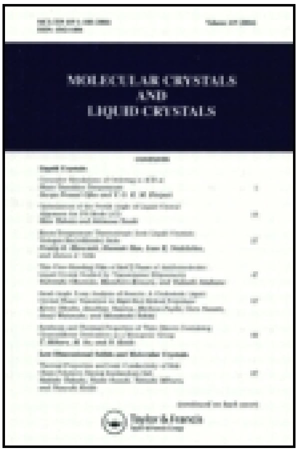

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Type of H-Bonded CT Complexes; [M(H_2DAG)(HDAG)]TCNQ (M = Ni,Pd,Pt)

Hiroshi Kitagawa [a] , Hiroshi Okamoto [a] , Tadaoki Mitani [a] & Masahiro Yamashita [b]

[a] Institute for Molecular Science, Okazaki 444, JAPAN

[b] Department of Chemistry, College of General Education, Nagoya University, Nagoya 464, JAPAN

Version of record first published: 24 Sep 2006.

To cite this article: Hiroshi Kitagawa , Hiroshi Okamoto , Tadaoki Mitani & Masahiro Yamashita (1993): New Type of H-Bonded CT Complexes; [M(H_2DAG)(HDAG)]TCNQ (M = Ni,Pd,Pt), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 228:1, 155-160

To link to this article: http://dx.doi.org/10.1080/10587259308032153

Mol. Cryst. Liq. Cryst. 1993, Vol. 228, pp. 155–160
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

NEW TYPE OF H-BONDED CT COMPLEXES; $[M(H_2DAG)(HDAG)]TCNQ$ (M=Ni,Pd,Pt)

HIROSHI KITAGAWA, HIROSHI OKAMOTO, and TADAOKI MITANI
Institute for Molecular Science, Okazaki 444, JAPAN

MASAHIRO YAMASHITA
Department of Chemistry, College of General Education, Nagoya University, Nagoya 464, JAPAN

Abstract The optical, electrical conductivity, and X-ray photoelectron spectroscopy measurements on $[M(H_2DAG)(HDAG)]TCNQ$ (M=Ni,Pd,Pt, H_2DAG=diaminoglyoxime) have been made. The results show unusual behavior around 250 K. The optical and transport properties are discussed.

INTRODUCTION

Since the discovery of organic metal in TTF-TCNQ, a large number of new organic metals have been synthesized and some of them exhibit superconductivity. Most of the organic metals contain segregated parallel stacks of planar organic donor and acceptor ions with a fractional average charge per molecule. On the other hand, there have been a large number of materials researches for highly conductive 1-D transition-metal complexes as such $K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 3H_2O$. The variety of these complexes is poor as compared to organic metals and superconductors have been scarcely discovered in the materials of this type until now.

We propose a two-band system as shown in Fig.1; a hybrid system composed of 1-D transition-metal-complex chains and 1-D organic acceptor (or donor) chains as mentioned above are coupled to each other through interband H bridges. The formation of the H-bond networks in solids provides a unique opportunity for construction of novel molecular assemblies, in which many electronic systems are combined *via* H-bond system[1]. And also this formation is expected to stabilize the structure of segregated stacks.

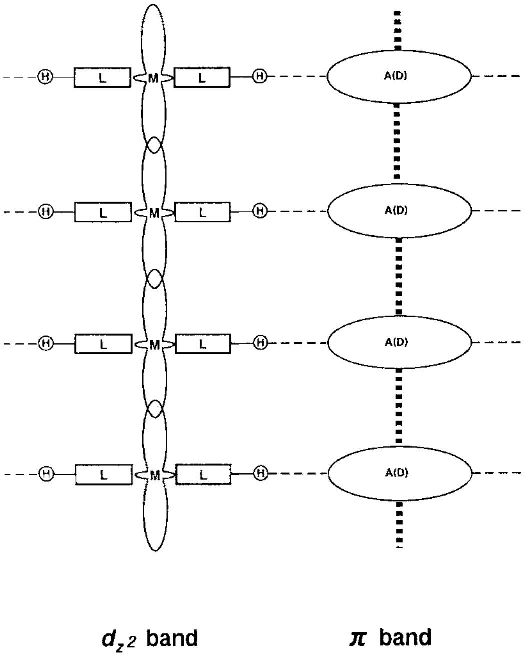

Fig.1 Two-band system of dz^2 and π bands.

When the partial CT occurs between the chains, *d* holes (or electrons) in the metal-complex chains and π electrons (or holes) in the organic acceptor (donor) chains are expected to cooperate trough the interchain H bonds. As the first demonstration of this system, we have investigated single crystals of $[M(H_2DAG)(HDAG)]TCNQ^2$. These complexes consist of segregated stacks of bis(oxamidoximato)M(II) complex donors and TCNQ acceptors, whose chains are connected to each other by interchain H bonds.

EXPERIMENTAL

All the single crystals were prepared by diffusion methods. The dc electrical-conductivity measurements were performed on single crystals with a four-probe method. For absorption spectra, powdered samples were diluted with KBr and then the mixtures were processed into pellets under pressure. The absorption spectra were measured in the temperature range 10-350 K with a Nicolet FTIR 800 or a Jasco CT-25C spectrometer. The X-ray photoelectron spectra were obtained in the temperature range 165-300 K on a VG ESCA MKII electron spectrometer, the source vacuum being ≈ 10^{-9} Torr. with Mg-Kα X-ray source (1253.6 eV).

RESULTS AND DISCUSSION

Fig.2 shows the absorption spectra of [$M(H_2DAG)(HDAG)$]TCNQ (M=Ni,Pd,Pt) at r.t. Each of the complexes showed four absorption bands in the region from visible to infrared. Following the experimental results by Torrance *et al.*, the bands at 2.1 and 3.5 eV are assigned to be intramolecular excitations in TCNQ molecules and bands at 0.4 and 1.4 eV are due to intermolecular transitions. The band at 1.4 eV can be understood by the picture of the CT intermolecular excitation of an electron between $TCNQ^-$ ions. The band at 0.4 eV is a CT intermolecular excitation of an electron from an occupied $TCNQ^-$ to a neutral TCNQ molecule, which is

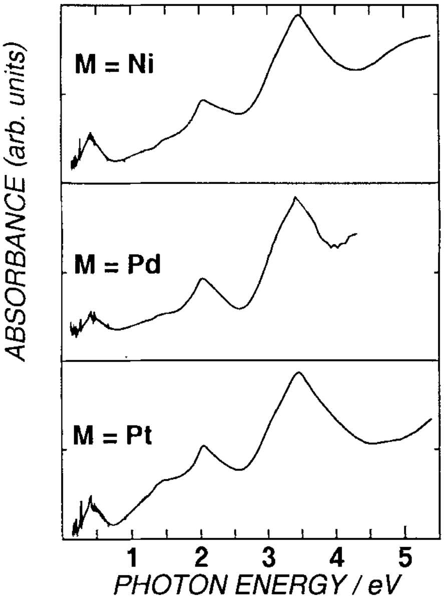

Fig.2 Absorption spectra of $M(H_2DAG)$(HDAG)]TCNQ at RT.

typically observed for highly conductive TCNQ salts such as TTF-TCNQ, NMP-TCNQ, Cs_2TCNQ_3, etc. These assignments lead to the conclusion that the $TCNQ^-$ stack exhibits mixed valency.

Fig.3 shows the IR absorption spectra of CN stretching vibrations for the Ni salt in the temperature range 18-338 K. The Pd and Pt salts showed similar IR spectra and temperature dependencies of the Ni salt. Around the room temperature CN stretching vibration is a triplet but in the temperature region below 240 K new three additional peaks appeared. In the region of 1000-2000 cm^{-1}, A_g-mode absorptions of TCNQ molecules are activated remarkably. The activation of A_g modes at low temperature implies these salts undergoes some lattice distortion such as a dimerization of $TCNQ^-$ ions or disordering of the H bonds.

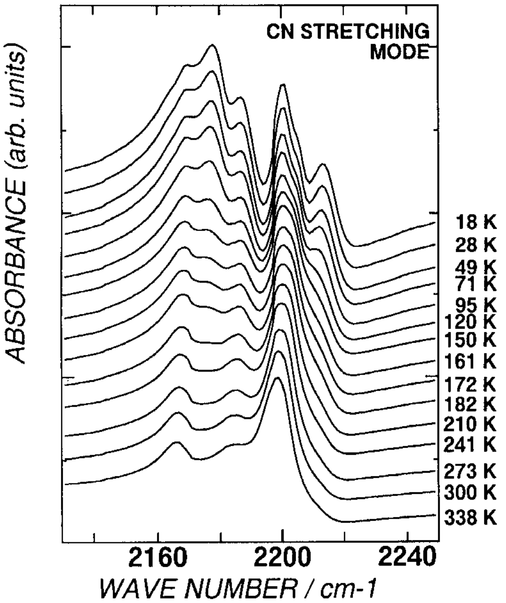

Fig.3 IR absorption spectra of CN stretching vibrations for the Ni salt.

As expected from the optical spectra, all of these salts are considerably highly conductive at room temperature. Temperature dependencies of the electrical resistivity parallel to the *a*-axis for Ni and Pt have been measured. All salts showed metallic behavior above around 270 K and semiconducting behavior at low temperatures. The resistivities of Ni and Pt salts at room temperature are almost same (≈ 1 Ω•cm) and the activation energies *Ea* of them are *ca.* 50 meV (between 100-250 K). It is noted that the behavior of resistivity exhibits a strong sample-batch dependency. Rather, it may be worthwhile to mention that these salts are sensitive to the condition of the preparation, *e.g.*, pH, or oxygen in air. The metal-to-semiconductor transitions can be considered to be related to the activation of A_g modes and the appearance of three new peaks in the IR spectra of CN stretching vibrations.

Fig.4 shows the XPS spectra in the Pt 4f region of the Pt salt at 165 K and r.t. As can be seen, the observed spectrum at r.t. is a typical Pt^{II} doublet, while that at

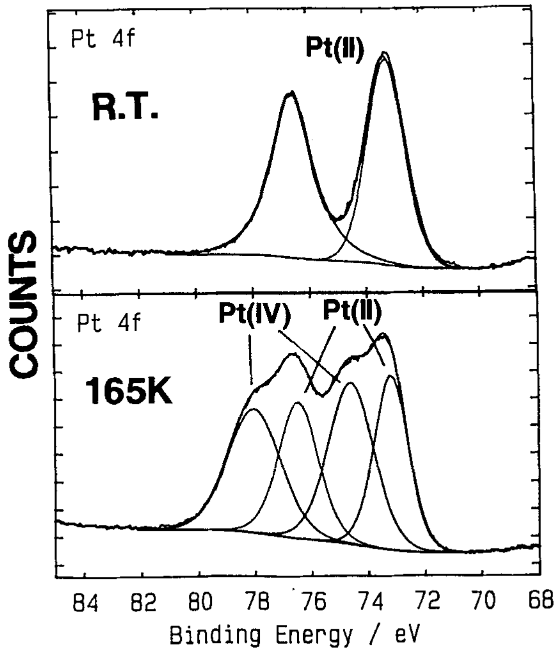

Fig.4 XPS spectra in the Pt 4f region of the Pt salt at r.t.(above) and 165 k(below).

165 K can be resolved into signals for Pt^{II} and Pt^{IV}, the latter ionizing at higher energy. The intensity ratio of Pt^{II} and Pt^{IV} components is *ca.* 1.0. The valence state of Pt in $[Pt(H_2DAG)(HDAG)]TCNQ$ changed from II to II-IV mixed-valence state in the low temperature below about 250 K. Also in the process upon increasing temperature, this drastic change of the Pt valence state was reproduced completely. This reproducibility indicates no X-ray beam effect on the sample. The similar phenomenon was observed for the Pd salt but not for Ni salt. It might be considered that this phenomenon is due to the charge transfer from the transition-metal-complex donor chain to the TCNQ acceptor one below about 250 K. When the charge transfer occurs, Pt or Pd in $[M(H_2DAG)(HDAG)]$ exhibits + III state but + II-IV mixed valency because of an instability of the valence state of Pt^{III} or Pd^{III}. It should be also mentioned that this anomalous phenomenon showed a sample-batch dependency as well as the electrical conductivity.

From the experimental results mentioned above, the TCNQ stack of each salt exhibits a partial oxidation state, and mainly contributes to the high conductivity around room temperature. The semiconducting behavior in the low-temperature region may arise from strong electron-lattice (or -proton) interaction; the CN stretching mode shows a characteristic temperature dependence below the temperature of the metal-to-semiconductor transition. In the case of Pd and Pt salts, anomalous changes occur in the valence state of M around the transition temperature. These anomalous phenomena described above require further detailed researches.

REFERENCES

1. T.Mitani, Mol.Cryst.Liq.Cryst.,171 (1989) 343.
2. H.Endres, Angew.Chem.Int.Ed.Engl.,21 (1982) 524.