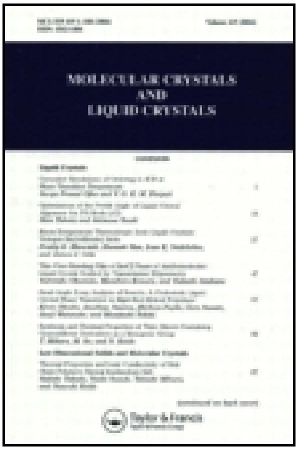


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structural and Electrostatic Modulation by Hydrogen Bonds Upon the Conduction Column of Ni(dmit)$_2$ Complex

Akira Miyazaki [a] , Akira Izuoka [a] & Tadashi Sugawara [a]
[a] Dept. of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Akira Miyazaki , Akira Izuoka & Tadashi Sugawara (1992): Structural and Electrostatic Modulation by Hydrogen Bonds Upon the Conduction Column of Ni(dmit)$_2$ Complex, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 217-222

To link to this article: http://dx.doi.org/10.1080/10587259208028776

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 217–222
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

STRUCTURAL AND ELECTROSTATIC MODULATION BY HYDROGEN BONDS UPON THE CONDUCTION COLUMN OF Ni(dmit)$_2$ COMPLEX

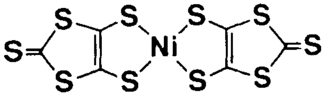
AKIRA MIYAZAKI, AKIRA IZUOKA and TADASHI SUGAWARA
Dept. of Pure and Applied Sciences, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153 Japan

Abstract In order to discuss the effect of dynamic modulation caused by hydrogen-bonded system on the conduction property, two Ni(dmit)$_2$ salts were prepared. In morpholinium salts a remarkable structural modulation was observed on the hydrogen-bonded Ni(dmit)$_2$ molecules. In the crystal of hydrated lithium salts, the hydrogen-bonded cation system is incorporated in a cylindrical channel constructed by corrugatedly stacked Ni(dmit)$_2$ columns, and a distinct hysteresis was observed on the temperature dependence of conductivity.

INTRODUCTION

If a hydrogen-bonded system, which has a possibility to show some dynamic processes, is incorporated in molecular conductors, conduction columns in crystals will be involved in hydrogen bond network. Thus the conduction columns ought to be modulated structurally and/or electrostatically, and new properties might appear. Such a system can be constructed by using hydrogen-bonded polymeric cations as a counter ion system in an anionic conductor. In order to ensure a linkage between the conduction column and the counter ion system, Ni(dmit)$_2$ was selected because it has proton acceptor sites (>C=S group).

Here we report preparation and crystal structure of two kinds of Ni(dmit)$_2$ complex with a hydrogen-bonded cation system and discuss the effect of structural and dynamic modulation on the conduction property.



Ni(dmit)$_2$

EXPERIMENTAL

Samples were prepared by galvanostatic (I=1μA) electrochemical oxidation of n-$Bu_4N[Ni(dmit)_2]$ (2mM). For morpholinium salt, oxidation was performed in the presence of morpholinium tetraphenylborate (50mM) as a supporting electrolyte in acetonitrile solution (25mL). For hydrated lithium salt, $LiClO_4$ (200mM) in acetonitrile:water (16:1) solution was used instead. Both elongated black plates grew on a platinum plate anode in a few days.

Crystal structure of the salts were determined by X-ray diffraction method. Crystal was mounted on a Rigaku AFC-5 four-circle diffractometer. *Morpholinium salt:* Monoclinic, $P2_1/n$, a=8.465(3), b=37.53(2), c=7.643(2)Å, β=92.59(2)°, V=2497(1)Å^3, Z=2. Final R=0.057 for 2220 reflections. *Hydrated lithium salt:* Orthorhombic, $C222_1$, a=41.70(2), b=11.321(5), c=11.305(9)Å, V=5337(6)Å^3, Z=12 for $Ni(dmit)_2$ molecules. Final R=0.093 for 1916 reflections. Both structures were solved by direct methods using the program *SAP185*[1], refined by a block-diagonalized least-squares method using *UNICS*-III system[2].

DC conductivities were measured along the elongated direction of the samples, using a four-probe method. Contacts of gold wires (diameter 25mm) were made by gold paint.

RESULTS

Morpholinium Salt: $(HMorph)_2[Ni(dmit)_2]_3$

In the crystal of the salt, morpholinium construct a one-dimensional hydrogen-bonded chain (Figure 1a). The equatorial hydrogen atom (H_{eq}) lies on the O-N-S plane and constructs a bifurcated hydrogen bond among oxygen atom in the morpholine ring and sulfur atom of thiocarbonyl group of dmit ligand (N···O: 2.82(1)Å, N···S: 3.33(1)Å), while the axial hydrogen atom on N (H_{ax}) forms a hydrogen bond to the thiocarbonyl group of another dmit ligand (N···S: 3.27(1)Å. Figure 1b). These two N···S lengths are shorter than usual value (mean value for N···S: 3.42(11)Å [3]), suggesting the presence of strong hydrogen bonds. As for the conduction column, two third of $Ni(dmit)_2$ molecules are remarkably deviated from the molecular plane due to these hydrogen bonds. As the result the conduction column is "trimerized".

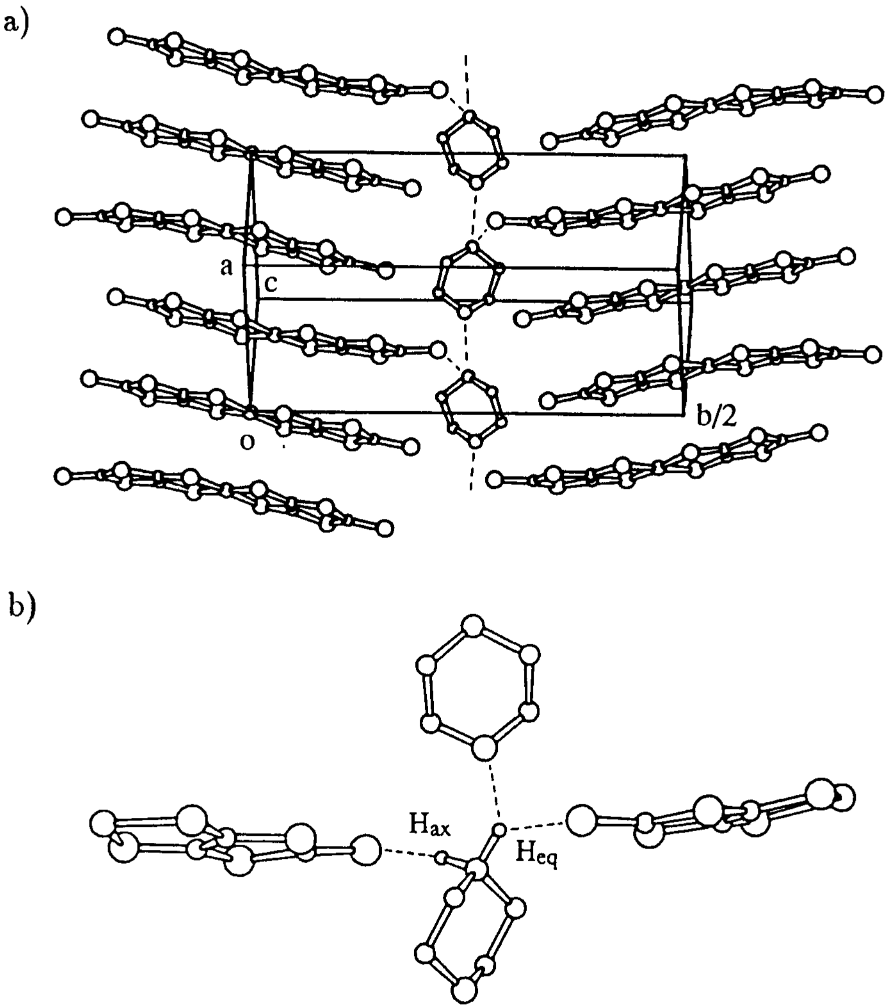


FIGURE 1 a) Crystal structure of morpholinium salt
b) Hydrogen-bonding scheme of morpholinium ion

The above crystal structure confirms that Ni(dmit)$_2$ molecules are incorporated in the hydrogen-bonded network and suffer from the structural modulation significantly. This salt behaves as a semiconductor (σ_{rt} =0.07Scm^{-1}, E_A=0.1eV), and no unusual behavior of conductivity was observed down to 100K.

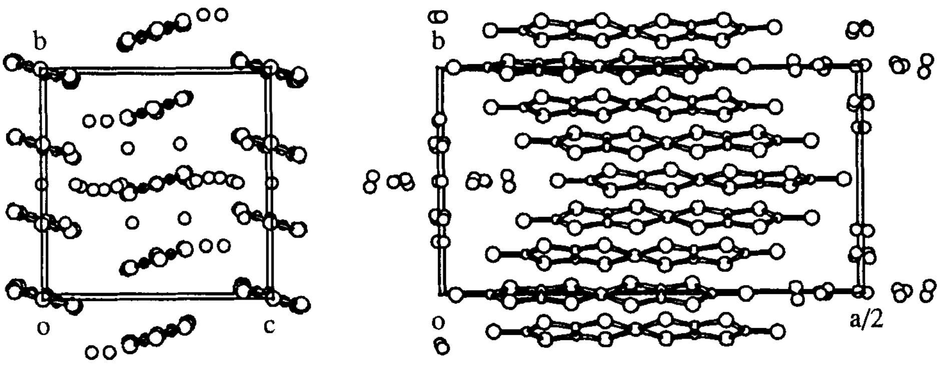


FIGURE 2 Crystal structure of hydrated lithium salt

Hydrated Lithium Salt: $Li_mNi(dmit)_2•(H_2O)_n$

We have adopted water clusters which contain lithium ions as a kernel: A high affinity of lithium ion to oxygen atoms guarantees formation of a hydration scheme.[4] If lithium cation and water molecules coexist in a solution at the time of crystal growth, hydrated lithium cation, i.e. lithium-water clusters can be incorporated into the crystal as a counter cation, with an aid of hydrogen bonds between water and thiocarbonyl group of dmit ligand.

Within the crystal, $Ni(dmit)_2$ molecules are stacked along the *b*-axis to form zigzag columns (Figure 2). There are cylindrical channels between these columns, and a number of peaks are recognized on ΔF-map within the channel. These peaks can be ascribed to oxygen atoms of incorporated water molecules. Some of waters are located in the center of the channel, while the others are close to the thiocarbonyl group of dmit ligand (~3.0Å from S). The distances among the oxygens are relatively small (2.5~3.0Å), which suggests that these molecules are hydrogen-bonded to each other. Presumably, lithium cation is located at the center of the cylinder and surrounded by double-layered water molecules. The resulted clusters are elongated perpendicular to the conduction column. The hydration pattern of cation might be analogous to that of $Li(H_2O)_3{\bullet}ClO_4$[5], in which lithium ions construct a chain bridged by water molecules.

Although sample dependency are large, the conductivity of the salts are reasonably high (σ_{rt}=0.2~20Scm^{-1}), and both the semiconductive(E_A=0.02eV) and metallic sample was obtained within the same batch. No significant difference of cell parameters between them suggests that their structural difference is subtle if any. In a plot of resistivities of the salts, a hysteresis loop was observed. Namely, the trace shows no unusual behavior with lowering temperatures, but with raising temperatures a distinct deviation was observed from the trace of the lowering process. This phenomenon appeared reproducibly on cooling-warming cycles. The degree of deviation is larger for the samples with higher conductivities. It might be reasonable to assume that there are metallic and semiconductive domains within one crystal and the anomaly comes from the metallic domains. Probably the water cluster seem to melt at around 200-250K on the warming process, and this causes a change in the hydration scheme structurally and/or electrostatically, which affects the metallic transport of the conduction electron.

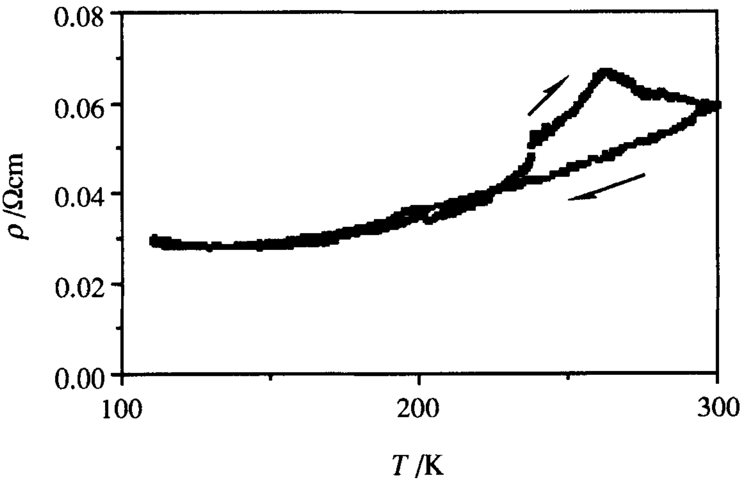


FIGURE 3 Electrical resistivity of hydrated lithium salts

CONCLUSION

In the morpholinium ion salts, a remarkable structural modulation was observed on the conduction column which is incorporated in the hydrogen-bonded counter ions. When hydrated lithium was chosen as the counter ion system, a hysteresis was observed on the conducting property of hydrated lithium salt. It may be reasonable to assume that a change of the hydration scheme causes this anomaly. Further analysis and determination of the origin of this phenomenon are in progress.

ACKNOWLEDGMENT

This study was partly supported by Grand-in-aid 02453006 from Ministry of Education, Science and Culture, Japan.

REFERENCES

1. H.-F. Fan, J.-X. Yao, J.-Z. Qian, *Acta Cryst.*, **A44**, 688-691 (1986)
2. T. Sakurai, K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69-77 (1979).
3. L. N. Kuleshova, P. M. Zorkii, *Acta Cryst.*, **B37**, 1363-1366 (1981).
4. U. Olsher, R. M. Izatt, J. S. Bradshaw, N. K. Dalley, *Chem. Rev.*, **91**, 137-164 (1991).
5. A. Sequeira, I. Bernal, I. D. Brown, R. Faggiani, *Acta Cryst.*, **B31**, 1735-1739 (1975)