Available online at www.sciencedirect.com

ScienceDirect

Inorganica Chimica Acta 361 (2008) 269–278

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Similar structural feature observed in the crystal packing of [Ni(dmit)$_2$] salts of geometrical isomer of methoxycarbonyl pyridinium

Kazuaki Tomono *, Kazumi Ogawa, Yuka Sasaki, Kazuo Miyamura *

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

Received 5 June 2007; received in revised form 25 July 2007; accepted 25 July 2007

Abstract

The crystal structures of the C–H···O hydrogen-bonded, 1:1 complex salts of with [Ni(dmit)$_2$]$^-$ 2MMP, 3MMP and 4MMP (*ortho*-, *meta*-, and *para*-methoxycarbonyl *N*-methyl-pyridinium, respectively) cations with have been investigated. All complex salts formed non-segregated stacks with the anions being sandwiched between layers or dimers of cations. Within these salts, the arrangement of the counter cations are structurally modulated by two weak intermolecular hydrogen bonds between the hydrogen of the pyridinium ring, methyl group or one of the two and the C=O group of the cations. The alignment of Ni(dmit)$_2$ molecules is found to be mainly governed by the attached position of methoxycarbonyl group. Powders of (2MMP)[Ni(dmit)$_2$], (3MMP)[Ni(dmit)$_2$] and (4MMP)[Ni(dmit)$_2$] salts exhibited room temperature conductivities of 4.33×10^{-10}, 1.80×10^{-6} and 5.60×10^{-6} S cm^{-1}, respectively.

Keywords: Nickel complexes; Dmit complex; Geometrical isomer of methoxycarbonyl pyridinium; Electrical conductivity; Crystal structure

1. Introduction

Transition metal complexes of dmit (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) have received significant attention since the report of the first open-shell molecular superconductor (TTF)[Ni(dmit)$_2$]$_2$ (TTF = tetrathiafulvalene) [1] and the first closed-shell molecular superconductor [N(CH$_3$)$_4$][Ni(dmit)$_2$]$_2$ [2]. Although the closed-shell cations make no contribution to the conductivity, their size and shapes play a predominant role in influencing the crystal structure and consequently in altering the electronic properties. Physical properties of molecular conductors depend on the molecular alignment in crystals. Unfortunately, the prediction of the molecular alignment within crystal is usually difficult, because of the presence of many local minima of lattice energy derived from van der Waals interaction which operates weakly and rather isotropically. On the other hand, hydrogen-bonding has a strictly fixed orientation, and this intermolecular interaction forms a characteristic structure in the crystal. The bonding schemes are therefore predictable to a certain extent [3,4]. Furthermore, the non-covalent intermolecular forces play a major role in determining the structures, i.e., especially of the biological macromolecules. As for the intermolecular interaction, the focus has been on the hydrophobic interaction; hydrogen bonds of the type X–H···Y (X = O, N and Y = O, N, halogen) are generally considered as major forces in the selective and/or specific molecular recognition. However, it has been increasingly recognized that weak interactions, such as C–H···O [5a,5b], C–H···S [6], C–H···N [7], C–H···π [8,9], N–H···C [10,11], cation···π [12,13], and anion···π [14] interaction, also play an important role in the stabilization of the aggregation structure (and also in the functions of biological macromolecules). We focused on such weak C–H···O, C–H···S hydrogen-bonds.

In fact, the Ni(dmit)$_2$ system has an advantage in this viewpoint, since dmit ligand has hydrogen bond accepting site (S groups). Thus, it seems interesting to investigate the effect of weak hydrogen bonds, but only few of the

---

* Corresponding authors. Tel.: +81 513 3260 4272; fax: +81 513 5261 4631 (K. Tomono).

E-mail address: 1303667@may.rikadai.jp (K. Tomono).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.07.021

Ni(dmit)$_2$ salts of cations involving carboxyl group (C=O) have been reported to data [15]. In this study, we have examined isomeric organic ions bearing both hydrogen donating and accepting sites, such as 2-methoxycarbonyl-1-methylpyridinium (2MMP), 3-methoxycarbonyl-1-methyl-pyridinium (3MMP) and 4-methoxycarbonyl-1-methylpyridinium (4MMP) ions, as a counter cation of the Ni(dmit)$_2$ complex. Such cations may reduce the spacing between the conductive anions and enhance the overlap of their molecular orbitals. In order to explore new dmit salts and gain more insight into the correlation between the structure and the hydrogen-bond [16], three complex salts mentioned above have been synthesized and their structures are investigated.

2. Experimental

2.1. Materials

n-Bu$_4$N[Ni(dmit)$_2$] was synthesised according to the literature [17]. 3-Methoxycarbonyl-1-methylpyridinium iodide and 4-methoxycarbonyl-1-methylpyridinium iodide was synthesised according to the references [15,18], respectively 2-methoxycarbonyl-1-methylpyridinium iodide was synthesized as follows: 2-methoxycarbonylpyridine (20 mmol) and methyl iodide (40 mmol) were refluxed in 20 ml dry Et$_2$O under N$_2$ for 3 days. The resultant solid was filtered and washed several times by Et$_2$O to give 2-methoxycarbonyl-1-methylpyridinium iodide. All reagents were of reagent grade and used without further purification.

2.1.1. Synthesis of (2MMP)[Ni(dmit)$_2$] (**1**)

The single crystal of 1 was prepared by the cation-exchange method and slow inter-diffusion of acetone solution (25 ml) of (Bu$_4$N)[Ni(dmit)$_2$] (0.05 mol) and chloroform solution (50 ml) of (2MMP)I (0.07 mol) at room temperature. Dark-green plate-like crystals of suitable size (typically 0.29 × 0.27 × 0.11 mm) for X-ray diffraction and for conductivity measurements were obtained after 3 days. *Anal.* Calc. for $C_{14}H_{10}NNiO_2S_{10}$: C, 27.85; H, 1.67; N, 2.32. Found: C, 27.36; H, 1.48; N, 2.23%. IR (KBr): 1740 cm^{-1} for ν(C=O), 1341 cm^{-1} for ν(C=C), 1063 cm^{-1} for ν(C=S).

2.1.2. Synthesis of (3MMP)[Ni(dmit)$_2$] (**2**)

(3MMP)$_2$[Ni(dmit)$_2$] was synthesized according to the general method of Steimecke et al. [17]. Single crystals of suitable size for X-ray diffraction and for conductivity measurements were grown in the following manner. The precipitate of (3MMP)$_2$[Ni(dmit)$_2$] was dissolved in acetone and oxidized using I$_2$ and NaI. Thin dark-green plate-like (typically 0.18 × 0.12 × 0.01 mm) crystals, one of which was used for the present structure determination, were obtained by slow evaporation. The compound was further purified by recrystallization from acetonitorile in air. *Anal.* Calc. for $C_{14}H_{10}NNiO_2S_{10}$: C, 27.85; H, 1.67; N, 2.32. Found: C, 27.76; H, 1.45; N, 2.13%. IR (KBr): 1726 cm^{-1} for ν(C=O), 1345 cm^{-1} for ν(C=C), 1064 cm^{-1} for ν(C=S).

2.1.3. Synthesis of (4MMP)[Ni(dmit)$_2$] (**3**)

The single crystal of 3 was prepared by the cation-exchange method and slow inter-diffusion of acetone solution (25 ml) of (Bu$_4$N)[Ni(dmit)$_2$] (0.05 mol) and chloroform solution (50 ml) of (4MMP)I (0.1 mol) at room temperature. Dark-green plate-like crystals of suitable size (typically 0.26 × 0.11 × 0.06 mm) for X-ray diffraction and for conductivity measurements were obtained after 2 days. *Anal.* Calc. for $C_{14}H_{10}NNiO_2S_{10}$: C, 27.85; H, 1.67; N, 2.32. Found: C, 28.00; H, 1.63; N, 2.35%. IR (KBr): 1724 cm^{-1} for ν(C=O), 1332 cm^{-1} for ν(C=C), 1075 and 1057 cm^{-1} for ν(C=S).

2.2. X-Ray data collection

Single crystal was mounted on a glass capillary. Intensity data were collected at 100(2) K by a Bruker AXS SMART diffractometer equipped with CCD area detector and Mo Kα ($\lambda = 0.71073$ Å) radiation [39]. The structures of **1**–**3** were solved and refined with the SHELX-97 [19] using direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogens isotropically. Selected crystallographic data for **1**, **2** and **3** are summarized in Table 1. The other crystal data for **1**: $\mu = 1.902$ mm^{-1}, 6844 reflections measured, 3380 unique ($R_{\text{int}} = 0.0278$), index ranges $-29 \leqslant h \leqslant 24$, $-9 \leqslant k \leqslant 10$, $-11 \leqslant l \leqslant 17$, $\Delta\rho_{\max} = 0.502$ e Å^{-3}, $\Delta\rho_{\min} = -0.308$ e Å^{-3}. For **2**: $\mu = 1.869$ mm^{-1}, 7209 reflections measured, 4870 unique ($R_{\text{int}} = 0.0464$), index ranges $-9 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 15$, $-10 \leqslant l \leqslant 16$, $\Delta\rho_{\max} = 1.676$ e Å^{-3}, $\Delta\rho_{\min} = -0.674$ e Å^{-3}. For **3**: $\mu = 1.932$ mm^{-1}, 7049 reflections measured, 4754 unique ($R_{\text{int}} = 0.0529$), index ranges $-7 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 10$, $-24 \leqslant l \leqslant 21$, $\Delta\rho_{\max} = 0.633$ e Å^{-3}, $\Delta\rho_{\min} = -0.383$ e Å^{-3}.

2.3. Measurements

The IR spectra (KBr pellets) were measured by a JASCO FT/IR-410 spectrophotometer. The elemental analysis data were obtained with a Perkin–Elmer 2400II CHN analyzer. Conductivity of the single crystals of **1**–**3** were measured at ambient pressure and room temperature using the two-probe method.

3. Results and discussion

3.1. Common structural feature and difference in crystal packing with substituted position of methoxycarbonyl group

3.1.1. Crystal structure of (2MMP)[Ni(dmit)$_2$] (**1**)

The asymmetric unit of **1** contains one crystallographically independent [Ni(dmit)$_2$]$^-$ anion and one cation as depicted in Fig. 1. The Ni–S distances range from 2.1606 (10) to 2.1673 (10) Å, with an average of 2.164 (1) Å, and