One-dimensional Strands of Trigonellinium Constructed by Intermolecular Strong O–H···O and Weak C–H···O Hydrogen Bonds in the Crystal of Partially Oxidized $Ni(dmit)_2$ Salt

Kazuaki Tomono* and Kazuo Miyamura
Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

(Received September 6, 2007; CL-070969; E-mail: 1303667@may.rikadai.jp)

The trigonellinium cations in the partially oxidized $Ni(dmit)_2$ complex salt **1** formed strong O–H···O hydrogen-bridged dimers, and the dimers are held together by the weak C(sp^2 and sp^3)–H···O hydrogen bond to form 1D strands. Further assembly through weak C(sp^3)–H···O hydrogen bond and $\pi\cdots\pi$ interaction resulted in the formation of $Ni(dmit)_2$ column structure.

Among various intermolecular interactions, hydrogen bond is one of the most important noncovalent interactions. Since the hydrogen bond can provide practicable methods for design of molecules with specific topologies,[1] it is often used to construct novel supramolecular assemblies. In many cases, supramolecular assemblies are achieved not only by the strong hydrogen bonds such as O–H···O and N–H···O but also by the weak C–H···O hydrogen bonds and $\pi\cdots\pi$ interactions. The importance of C–H···O hydrogen bonds is now widely recognized especially in the formation of crystal structures. The understanding and utilization of all noncovalent interactions including allegedly weak interactions are of fundamental importance for further development of crystal engineering, i.e., the tuning and the prediction of crystal structure.[2]

The metal complex $Ni(dmit)_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) has been widely studied as conducting or magnetic materials.[3] Its molecular arrangement can be sensitively affected by strong and directional noncovalent interactions. To date, we have been exploring a method to control the $Ni(dmit)_2$ arrangement by regulating intermolecular interaction of chemically modified cations.[4] The synthesis of (3MMP)-[$Ni(dmit)_2$] (3MMP = *meta*(3)-methoxycarbonyl-1-methylpyridinium) has aroused our interest in weak hydrogen bond, because less attention has been paid to the ability of weak hydrogen bonds to control the arrangement of complex salts. In this report, we have used a trigonellinium ion (3-carboxy-1-methylpyridinium, TRGH) as a counter cation. TRGH is an OCH_3 to OH substituted 3MMP analogue, and we have expected a formation of three-dimensional network through O–H···O hydrogen bonds.[5] However, novel one-dimensional (1D) strands of trigonellium cations are formed through cooperative weak and strong hydrogen bonds. To the best of our knowledge, regardless of small planar cation used, this complex salt is the first example of the aggregate constructed by the cooperation of weak and strong hydrogen bonds in the $Ni(dmit)_2$ salt.

The single-crystal X-ray diffraction analysis[6] showed that the complex salt **1**[7] is constituted of crystallographically independent three $[Ni(dmit)_2]^{0.5-}$ and three trigonellinium as counter cations. Two trigonellinium share one hydrogen atom (H2) by two carbonyl oxgen atoms. The remaining trigonellinium together with its symmetrically equivalent one also shares one hydrogen atom (H4) (see Figure 1a). However, owing to the symmetric requirement, H4 is treated as a disorder with 50% population. Packing analysis revealed the formation of 1D strand constructed by weak and strong hydrogen bonds. Three strands are stacked to form rod-like structure as shown in Figures 1c and 1d. The hydrogen bonds O–H···O of H2 and H4 [O(4)···O(4A) = 2.487(6) Å, O2···O6 = 2.468(4) Å; O(4)–H(4)–O(4A) = 176°, O(2)–H(2)–O(6) = 157°] known as the low-barrier hydrogen bonds (LBHB) are especially strong.[8] Furthermore, the dimers formed by this LBHB are linked by weak C(sp^2 and sp^3)–H···O hydrogen bonds [2.25–2.65 Å (H···O), 3.054(6)–3.377(6) Å (C···O), 132–150° for H4-linked dimer; 2.21–2.69 Å (H···O), 3.121(7)–3.508 Å (C···O), 129–168° for H2-linked dimer] to form planar and nonplanar 1D strands (Figure 1b; nonplanar strand is omitted for clarity.). In the C–H···O hydrogen bonds, typical values for H···O and C···O distances were 2.4–3.0 and 3.0–4.0 Å, respectively.[9] Furthermore, the planar and nonplanar strands are held together by C–H···O hydrogen bond and $\pi\cdots\pi$ stacking interaction to form the 1D rod-like domain oriented parallel to *a* axis as shown in

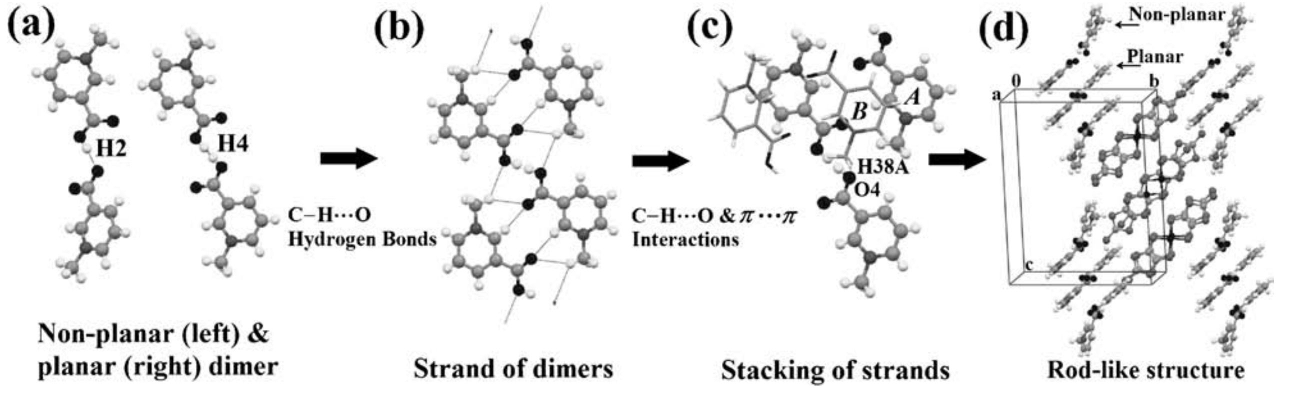

Figure 1. Packing scheme of **1**. Dashed lines indicate the intermolecular (a) O–H···O, (b) C(sp^2 and sp^3)–H···O, and (c) C(sp^3)–H···O hydrogen bonds. (d) Crystal structure of the salts **1**.

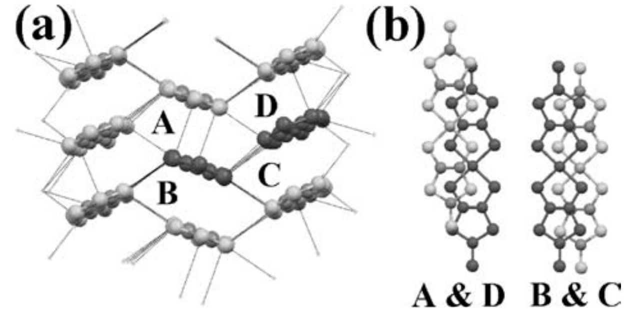

Figure 2. (a) Columns of Ni(dmit)$_2$. S···S distances shorter than 3.7 Å, the sum of the van der Waals distance, are shown by dotted lines. (b) Two modes of overlaps between the stacked Ni(dmit)$_2$ anions.

Figure 1c, where the capped-sticks style is used to express non-planar strand and the ball-and-stick style used for planar one. The geometric parameters are 2.70 Å (H(38A)···O(4)), 3.595 Å (C(38)···O(4)), 156°, and interplanar distance between **A** and **B** planes is 3.582 Å.[2a] As shown in Figure 1d, the diameter of the rod-like domain of strands of cations is ca. 21.1 Å. Although Ni(dmit)$_2$ anions are surrounded by the rods, inter-anionic contacts still remain in the directions of *b* and *c* axes.

Figure 2 shows the columns of Ni(dmit)$_2$ units viewed along *c* axis. There are no significant differences in the bond lengths and angles between the three independent Ni(dmit)$_2$ units. Since some vibration mode was known to be sensitive to the formal charge of Ni(dmit)$_2$, the IR spectra have been examined. The strong band around 1280 cm^{-1} observed is assigned to the C=C stretching band. This band was known to exhibit large shifts by the formal charge of Ni(dmit)$_2$; 1260 cm^{-1} for [Ni(dmit)$_2$]$^{0.29-}$, 1350 cm^{-1} for [Ni(dmit)$_2$]$^-$ and 1440 cm^{-1} for [Ni(dmit)$_2$]$^{2-}$.[3d] The result shows that the [Ni(dmit)$_2$] units are neither mono- nor dianion,[7] but are in a partially oxidized state, as can be estimated from the stoichiometry. Independent interplanar distances are 3.50 (**A**), 3.53 (**B**), 3.54 (**C**), and 3.60 (**D**) Å (see Figure 2a). The modes of the molecular overlaps are shown in Figure 2b. There are a large number of intermolecular S···S contacts between intra- and intercolumns which were known to be responsible for the high conductivity; the distance of S···S contacts between intra- and intercolumn in the directions of *a*, *b*, and *c* axes is in the range of 3.43–3.69, 3.47, 3.25–3.65 Å, respectively.

The electrical conductivity of compacted pellet[7] of **1** shows semiconducting behavior with room-temperature conductivity of 2.2×10^{-4} S·cm^{-1} which is lower by 10^2–10^4 compared with other partially oxidized Ni(dmit)$_2$ complex salts.[10] The reason of the low conductivity is uncertain, but the use of the compacted pellet instead of single crystal might have decreased the conductivity, since the preparation of large single crystal is unsuccessful. The anisotropy of the electrical conduction can be estimated from the 1D structure of the crystal. In the case of [(CH$_3$)$_4$N]-[Ni(dmit)$_2$]$_2$ which has smaller cation, the anisotropy of the electrical conductivity was about 10^3.[10d]

In conclusion, we have shown supramolecular synthon model for the construction of the 1D crystal structure based on cooperative weak and strong hydrogen bonds. The present result demonstrates that although the electrostatic interaction predominates and controls the crystal packing, the weak interaction also plays an important role in determining the orientation of the cations.

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6 Crystal data for **1**: $C_{26}H_{15}N_2Ni_2O_4S_{20}$, $M_r = 1178.02$, Triclinic, space group $P\bar{1}$, $a = 8.1752(5)$, $b = 17.8348(10)$, $c = 21.2690(13)$ Å, $\alpha = 88.703(1)°$, $\beta = 84.252(1)°$, $\gamma = 81.862(1)°$, $T = 100(1)$ K, $V = 3054.3(3)$ Å^3, $Z = 3$, $D_{\mathrm{calcd}} = 1.921$ Mg m^{-3}, $\mu = 1.990$ mm^{-1}, 21866 reflections collected, 14830 independent ($R_{\mathrm{int}} = 0.0282$), The final $R_1 = 0.0409$, $wR_2 = 0.0870$ [$I > 2\sigma(I)$]. CCDC 657103.

7 4,5-Bis(thiobenzoyl)-1,3-dithiole-2-thione was prepared according to the method reported in the literature: G. Steimecke, H. J. Sieler, R. Kirmse, E. Hoyer, *Phosphorus Sulfur.* **1978**, *7*, 49. 4,5-Bis(thiobenzoyl)-1,3-dithiole-2-thione (920 mg, 2.25 mmol) was suspended in methanol (10 mL). Sodium methoxide in methanol (prepared from 322 mg sodium in 7 mL methanol) was added to the above mixture at room temperature in 20 min to give a dark red solution. To this solution $NiCl_2 \cdot 6H_2O$ (238 mg, 1 mmol) was added. After 10 min, a solution of I_2 (127 mg, 1 mmol) and NaI (150 mg, 1 mmol) in methanol (20 mL) was added. After another 30 min, a solution of trigonelline hydrochloride (TRGH chloride; 870 mg, 5 mmol) in ethanol (50 mL) was added to the reaction mixture. Then, the solution was stirred for 20 min and cooled in a refrigerator for two days leading to the precipitation of thin black single-crystal of (TRG$_2$H)[Ni(dmit)$_2$]$_2$. The elemental analysis was performed with a Perkin-Elmer 2400II CHN Analyzer. Anal. Found: C, 26.46; H, 0.98; N, 2.46%. Calcd for $C_{26}H_{15}N_2Ni_2O_4S_{20}$: C, 26.50; H, 1.28; N, 2.37%. The IR spectra (KBr pellets) were measured by a JASCO FT/IR-410 spectrophotometer. IR (KBr, cm^{-1}): 3056 (w), 1719 (w, C=O), 1629 (w), 1315 (w), 1248 (s and br, C=C), 1065 (m), 1037 (m), 1017 (m), 922 (s), 759 (m), 671 (m), 509 (m). Conductivity measurements were carried out at ambient pressure using the two-probe method. The compacted pellets were measured at room temperature. The bond distances and angles were Ni–S (2.147–2.166 Å) and cis S–Ni–S (85–93°), respectively, indicative of partially oxidized state.

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