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水素結合した(H-DABCO)₂(DABCO)三量体を含む[Ni(dmit)₂]結晶の構造と物性

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Crystal Structure and Physical Properties of [Ni(dmit)₂] Salt of Hydrogen Bonded (H-DABCO)₂(DABCO) Trimer

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【Introduction】

Molecular electronic materials have attracted intensive attention due to their merits of finely-controlled physical properties, reduction in primary materials and thus economic and friendly for the environment. In recent decades, various materials have been designed, synthesized and characterized, which enrich the electronics family and enable us to investigate them deeply[1].

In the continuous effort to develop novel electronic and magnetic materials in molecular scale, here two novel compounds, named (H⁺-DABCO)₂(DABCO)[Ni(dmit)₂]₂ (**1**) and (H⁺-DABCO)₅(DABCO)[Ni(dmit)₂]₅ (**2**) have been synthesized by mixing [Ni(dmit)₂]⁻ (dmit₂⁻ = 1,3-dithiole-2-thione-4,5-dithiolate) and protonated cation of DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane). Detailed study on their crystal structure, magnetic and dielectric properties are reported.

【Results and Discussion】

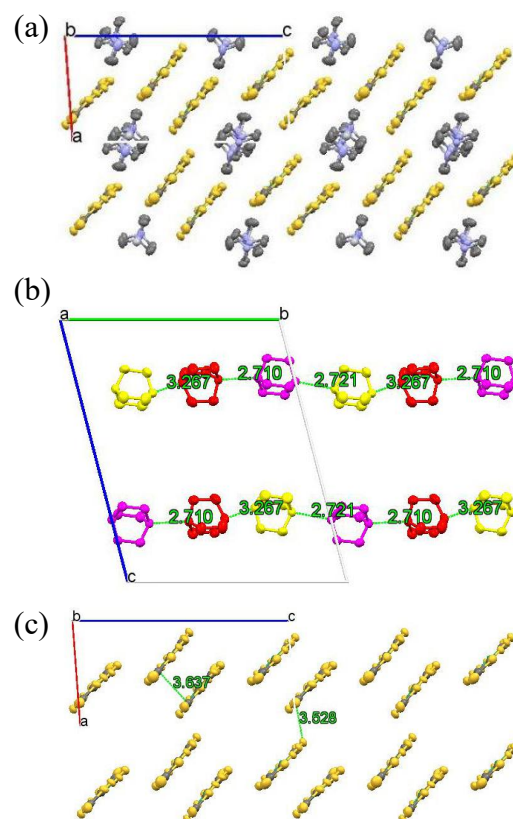


Figure 1. Crystal structure of **1**. (a) Packing structure viewed along the *b* axis. (b) DABCO trimer with the intermolecular N...N distances. (c) [Ni(dmit)₂] arrangement.

The synthesis of **1** involves mixing of (H-DABCO)(BF₄) and (tetra-*n*-butylammonium)⁺[Ni(dmit)₂]⁻ in acetonitrile, while the compound **2** in acetone. Black crystals were obtained after natural evaporation of the solutions. X-ray single crystal analyses reveal that both crystals **1** and **2** belonged to space group *P*-1. As shown in Fig.1b and Fig.2b, the distances between intermolecular nitrogen (N) atoms were 2.710, 2.721, and 3.267 Å for the crystal **1** and 2.802, 2.759, 2.712, 2.759, 2.802 and 3.232 Å for the crystal **2**. Since the bonds with length less than 3.2 Å can be assigned as moderate hydrogen bonds, formation of trimer of (DABCO)₃ with two protons, [H₂(DABCO)₃], and hexamer with five protons, [H₅(DABCO)₆], was suggested for **1** and **2**, respectively. Crystallographically independent [Ni(dmit)₂]⁻ anions in the crystal **1** were dimerized with the nearest carbon (C)•••C distance of 3.637 Å. Each dimer unit was interacted through sulfur (S)•••S contacts with the distance of 3.528 Å along the *+a*-*b* direction in **1** (Figure 1c). In the crystal **2**, five [Ni(dmit)₂]⁻ anions were crystallographically independent, and they aligned two-dimensionally. Four of five were parallel to each other, while one of them was aligned with the angle about 60° to the assembly (Figure 2c).

Dielectric measurement of **1** exhibited temperature- and frequency-dependent peaks in imaginary part of dielectric constant (ϵ_2), suggesting molecular motions. On the other hand, crystal **2** showed a rapid increase in ϵ_2 with increasing temperature above 200 K, indicating semiconducting nature of the crystal. The crystal **1** showed a singlet-triplet-type temperature dependence of spin susceptibility. On the other hand, increase of $\chi_m T$ value with decreasing temperature was observed for crystal **2**, suggesting ferromagnetic interaction.

【Reference】

[1] T. Akutagawa et al., *J. Am. Chem. Soc.* **2004**, 126, 291.

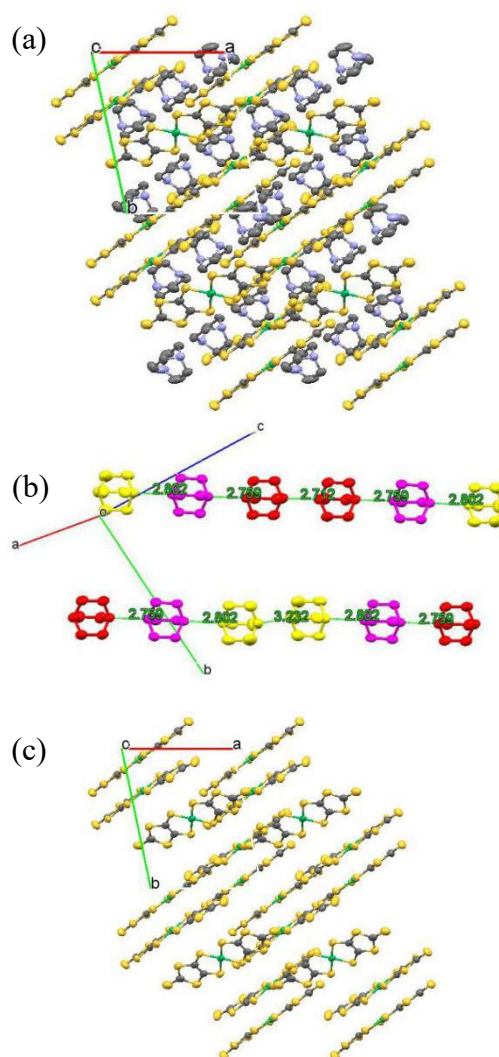


Figure 2. Crystal structure of **2**. (a) Packing structure viewed along the *c* axis. (b) DABCO hexamer with the intermolecular N•••N distances. (c) [Ni(dmit)₂]⁻ arrangement.