Anomalous Distortion and Stacking Column Formation of $[Ni(dmit)_2]^-$ Induced by Propeller-Shaped Dye Cations, Crystal Violet and Basic Fuchsin

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$(CV^+)[Ni(dmit)_2]\cdot 1/2(C_6H_6)$ (**1**) and $(BF^+)[Ni(dmit)_2]$ (**2**) (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato, CV^+ = cation of Crystal Violet, BF^+ = cation of Basic Fuchsin) were prepared and characterized by X-ray crystal structural analysis. In the crystal structure of **1**, the $Ni(dmit)_2$ unit was bent at Ni in a V shape with an angle of 13.7° and tetrahedral distortion of 8.8° around Ni was also present that originated from the steric effect of the propeller-shaped CV cation. In the case of **2**, BF and $[Ni(dmit)_2]^-$ formed an independent stacking column in which $[Ni(dmit)_2]^-$ were stacked alternately rotated with an angle of 90° to each other. **1** and **2** exhibited semiconducting behavior with room-temperature conductivities of 2.9×10^{-7} and 9.0×10^{-5} $S\,cm^{-1}$, respectively.

The metal–dithiolate complex is an excellent building block for electronic functional materials. Seven molecular superconductors based on $M(dmit)_2$ have been discovered.[1] The counter cations used in the molecular conductors can be closed shell cations as well as open shell ones. However, the cations used are mostly closed shell ones and a small number of aromatic compounds have been employed as the counter cations. Recently, Cornelissen et al. reported $(tmiz)[Ni(dmit)_2]$ (tmiz = 1,2,3-trimethylimidazolium) salt featuring a type of cation that can be regarded as an intermediate between an open shell and closed shell cation. This compound showed a high conductivity of $0.21\,S\,cm^{-1}$ compared with other monoanionic $Ni(dmit)_2$ complex salts.[2] $(MeQ)[Ni(dmit)_2]$ (MeQ = *N*-methylquinolinium) was characterized by X-ray crystal structural analysis and exhibited a conductivity of $10^{-3}\,S\,cm^{-1}$.[3] These compounds crystallize in a non-segregated manner, displaying a face-to-face stacking mode of the anions and cations. These results suggested that the interaction between the π-electronic systems of both the cations and the anions might be responsible for the conductivity. In this work, we have selected triphenylmethane dyes, *N*-[4-[bis[4-(dimethylamino)phenyl]methylene]-2,5-cyclohexadien-1-ylidene]-*N*-methylmethanaminium (cation of Crystal Violet = CV^+) and tris(4-aminophenyl)methylium (cation of Basic Fuchsin = BF^+), as the counter cations of $[Ni(dmit)_2]^-$ (Chart 1). Basic Fuchsin and Crystal Violet have a basic structure of the triphenylcarbon group and this structure has a large planar conjugated π system. The vibrant colors of these dyes show potential electric and optic properties. However, the crystal structure of $CV^+Cl^-\cdot 9H_2O$ was determined and the propeller shape of the CV cation was confirmed.[4] Crystal Violet showed photoconductive behavior of $10^{-7}\,S\,cm^{-1}$ in a thin solid film.[5] Then, $[Ni(dmit)_2]^-$ complex salts of CV^+ and BF^+ were prepared and characterized by X-ray single-crystal structural analysis and electric conductivity.

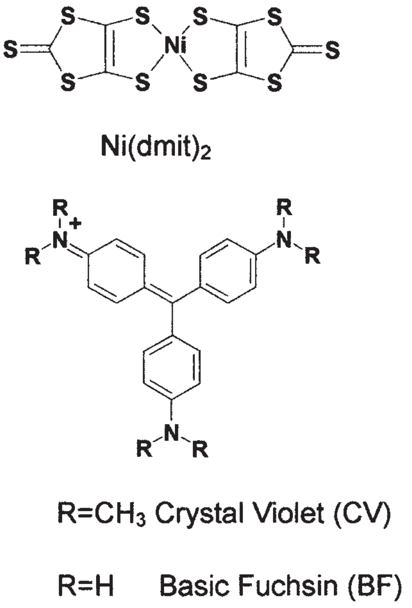

Chart 1.

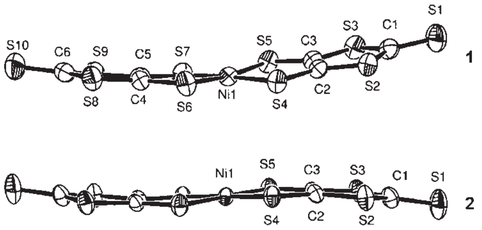

Fig. 1. Displacement ellipsoids of $[Ni(dmit)_2]^-$ in **1** and **2** were drawn at the 50% probability level.

The displacement ellipsoids of $[Ni(dmit)_2]^-$ in **1** with the labeling scheme are depicted in Fig. 1. The Ni–S bond distances were 2.1603(7)–2.1667(7) Å, being in good accord with the values found for $\{N(C_4H_9)_4\}[Ni(dmit)_2]$, which was regarded as a monoanion radical.[6] The $Ni(dmit)_2$ unit showed a large deviation from planarity. The $Ni(dmit)_2$ unit was bent at Ni in a V shape with the angle of 13.7° and tetrahedral distortion of 8.8° around Ni was also present. In the case of the complex salt of *N*-methylquinolinium, the NiS_4 coordination geometry of $[Ni(dmit)_2]^-$ was also bent at an angle of 5.24° and tetrahedral distortion of 2.14°.[3] The structures of dye cations were also distorted from planarity. Examination of molecular models revealed that the six *ortho*-hydrogen atoms, in Crystal Violet, were subjected to steric hindrance. In order to reduce this

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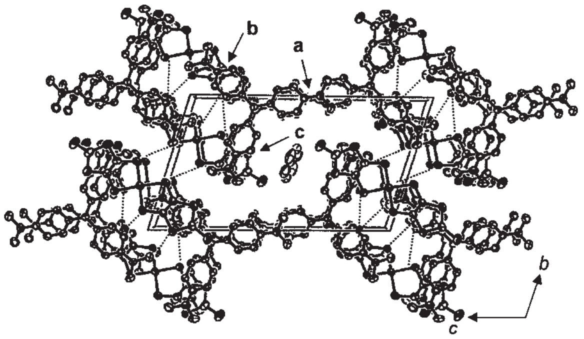

Fig. 2. Crystal structure of **1** viewed along the *a*-axis. The dotted lines indicate the S–S contacts shorter than 3.7 Å. Hydrophobic interactions of cation–cation (**a**) and cation–anion (**b** and **c**) were found and C=S distances at **c** [1.644(3) Å] were longer than that at **b** [1.632(3) Å].

effect, Crystal Violet adopted a propeller shape.[7] In the crystal structure of **1**, the anion complexes and CV cations were piled up alternately, which implied that the large distortion of $[Ni(dmit)_2]^-$ had originated from the steric effect of the propeller-shaped CV cation shown in Fig. 2. Lueck et al. proposed a dimer structure for the CV cation in which the dimethylamino groups overlapped in a head-to-tail manner suitable for maximizing the hydrophobic interactions.[8] In **1**, CV cations formed the head-to-tail dimer, but the overlap of the dimethylamino groups was smaller than that of $CV^+Cl^- \cdot 9H_2O$. Additionally, the distance of the overlapped plane between the intra-dimer in **1** was 3.56 Å longer than that of $CV^+Cl^- \cdot 9H_2O$ (3.42 Å) shown in Fig. 2**a**. Thus, the intra-dimer interaction was estimated to be weak. In $CV^+Cl^- \cdot 9H_2O$, the dihedral angles between aminomethyl groups and phenyl groups were 5.91 and 8.76°, respectively, while that of **1** was up to 17.96°, which was induced by the overlap with $[Ni(dmit)_2]^-$. This hydrophobic interaction of the cation and the anion induced the elongation of the C=S distance [1.644(3) Å], which was longer than that without cation–anion interaction [1.632(3) Å]. In **1**, three different inter-anion S–S contacts, shorter than the sum of the van der Waals radii, were found. The pairs of $[Ni(dmit)_2]^-$ combined with the distance of 3.544(1) Å (S2–S4 $[1-x, -y, -z]$), 3.612(1) Å (S2–S6 $[1-x, -y, -z]$) were located side by side, and the inter-pair distance was 3.642(1) Å (S5–S7 $[1-x, 1-y, -z]$). Thus, anions were connected along the *b*-axis as shown in Fig. 2. Since it was suggested that the orbital overlaps of anions effective for conduction were present at the side by side alignment or stacking within the distance of 3.7 Å, the electronic interaction was estimated to be relatively strong in **1**.

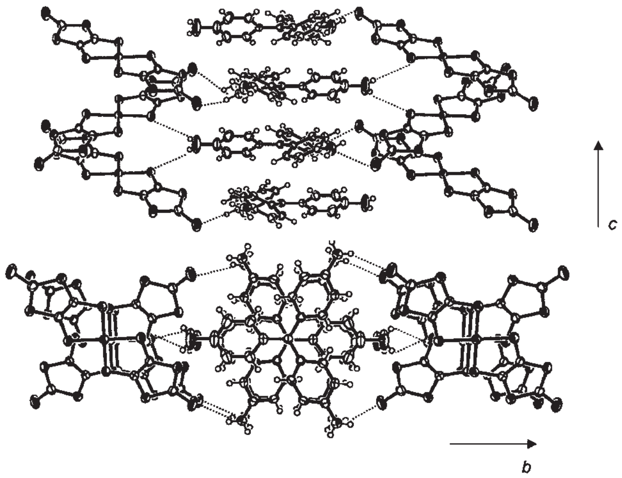

Fig. 3. Inter-column hydrogen-bond network of **2** viewed from different angles. The hydrogen bonds of N–H···S are represented by dotted lines.

Table 1. Parameters Hydrogen Bonds between N–H···S

D–H···A	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)–H(1B)···S(1)	2.86	3.343(3)	117.0
N(1)–H(1B)···S(1)	2.94	3.691(3)	147.1
N(1)–H(1A)···S(4)	3.01	3.427(3)	112.1
N(2)–H(1A)···S(5)	3.07	3.589(3)	120.2

The displacement ellipsoids of $[Ni(dmit)_2]^-$ in **2** with the labeling scheme are depicted in Fig. 1. The Ni1–S5 bond distance [2.1725(9) Å] was longer than those of general mono-anionic complexes. This occurs by the contact of S5 with the ligand center C atoms of the sandwiched $[Ni(dmit)_2]^-$ anion with the distance of 3.433(3) Å (S5–C2′ $[-x, y, 1.5-z]$) and 3.407(3) Å (S5–C3′ $[-x, y, 1.5-z]$). The conformation geometry around NiS_4 was essentially planar, but the dmit ligand was bent in a V shape with the angle of 7.5° due to the hydrogen bond between the N–H of BF^+ and the terminal S atom of $[Ni(dmit)_2]^-$. The organic cation had a propeller shape, just like its shape in the crystal of a perchlorate described by Koh et al., and intramolecular bond lengths and angles of the BF cation represented no significant change.[9] $[Ni(dmit)_2]^-$ and BF^+ formed independent stacking columns along the *c*-axis, similar to the case of $[Ni(dmit)_2]^{n-}$ $(0 < n < 1)$ complex salts, which form stacking columns. However, the structure of the $[Ni(dmit)_2]^-$ column was different. In the stacking column of **2**, $[Ni(dmit)_2]^-$ were stacked alternately rotated with an angle of 90° to each other in the columns shown in Fig. 3. This stacking structure is similar to that observed for $Ni(dpg)_2I$ (dpg = diphenylglyoximato), where the $[Ni(dpg)_2]$ units were stacked alternately rotated with an angle of 90°.[10] $Ni(dmit)_2$ complex salts that contains a π-conjugated cation and in which the cation/anion ratio is 1, usually form non-segregated stacks with the cation and anion as **1**.[2,3] As shown in Fig. 3, the hydrogen bonds of N–H···S were present at all $[Ni(dmit)_2]^-$ so that the columns of $[Ni(dmit)_2]^-$ and BF^+ were bound firmly. The parameters were tabulated in Table 1. Since this crystal structure was controlled by these hydrogen bonds, the $[Ni(dmit)_2]^-$ could form an independent stacking column. The S–S contact was also found with the distance of 3.620(2) Å (S3–S3′ $[-x, y, 1.5-z]$).

The electric conductivities of single crystals of **1** and **2** were measured by the two probe method. Both complex salts exhibited semiconducting behavior in the temperature range of 268 to 373 K with room-temperature conductivities of 2.9×10^{-7} and 9.0×10^{-5}, respectively. In **1**, the interaction between $[Ni(dmit)_2]^-$ and CV^+ was found, but the electric conductivity was not as high as expected. The reason is uncertain, but the anomalous distortion of $[Ni(dmit)_2]^-$ might be the reason for this low conductivity. In the previous report,[11] however, the crystal of the 3-(4- and 3-alkyl-pyridinium)-1,5-diphenylverdazyl radical cation, which was similar to the triphenylmethane dyes, with Ni(dmit)$_2$ formed in a non-segregated manner, and the electric conductivity of these compounds were as high as 10^{-3}–10^{-6} S cm^{-1}, similar to that of **2**. In (BF)[PMo$_{12}$O$_{40}$]•3H$_2$O, an unpaired electron was generated via a charge-transfer mode from the organic cation to the polyanion.[12] The μ_{eff} of **2** measured with MSB-MKI (Sherwood Scientific LTD Cambridge, England) was 1.87 (emu K mol^{-1}), which was a normal value for localized [Ni(dmit)$_2$]$^-$. Thus, the stacking column structure should be responsible for the relatively high conductivity of **2**, and not the charge transfer between the cations and anions.

Experimental

Preparation of (CV)[Ni(dmit)$_2$]•1/2(C$_6$H$_6$) (1) and (BF)-[Ni(dmit)$_2$] (2). 4,5-Bis(thiobenzoyl)-1,3-dithiole-2-thione was prepared according to the detailed procedures described by Steimecke et al.[13] (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 for 20 min to give a dark red solution. To this solution NiCl$_2$•6H$_2$O (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 10 min, a solution of CV$^+$Cl$^-$•9H$_2$O (570 mg, 1 mmol) in methanol (50 mL) was added to the reaction mixture. Then, the solution was stirred for 30 min and cooled in a refrigerator overnight. The precipitant was dissolved by a mixed hot solvent using acetonitrile and benzene, and then filtered. A day after, gold block crystals of **1** were obtained in the filtrate. **2** was synthesized by a similar way to **1** using BF$^+$Cl$^-$ (337 mg, 1 mmol). Green disk like crystals of **2** were obtained in the filtrate. The elemental analysis data were performed with a Perkin-Elmer 2400II CHN Analyzer. **1**: Yield, 0.21 g (25%). Anal. Found: C, 46.89; H, 3.40; N, 4.92%. Calcd for C$_{34}$H$_{33}$N$_3$NiS$_{10}$: C, 47.31; H, 3.85; N, 4.87%. **2**: Yield, 0.25 g (34%). Anal. Found: C, 40.91; H, 2.91; N, 5.94%. Calcd for C$_{25}$H$_{18}$N$_3$NiS$_{10}$: C, 40.59; H, 2.45; N, 5.68%.

X-ray Crystallography. A single crystal was mounted on a glass capillary, transferred to a Bruker AXS SMART diffractometer equipped with a CCD area detector and Mo Kα ($\lambda = 0.71073$ Å) radiation, and centered in the beam at 297 K. The structures were solved and refined with SHELX-97[14] using the direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogens isotropically. Crystal data for **1**: C$_{34}$H$_{33}$N$_3$NiS$_{10}$, $M_r = 862.94$, $a = 7.8380(5)$ Å, $b = 12.1436(7)$ Å, $c = 20.8824(12)$ Å, $\alpha = 106.2410(10)°$, $\beta = 97.6650(10)°$, $\gamma = 95.1480(10)°$, $V = 1874.32(19)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$, $T = 297(2)$ K, $D_{\text{calcd}} = 1.529$ Mg m^{-3}, $\mu = 1.106$ mm^{-1}, 12583 reflections measured, 8449 unique ($R_{\text{int}} = 0.0326$), GOF (on F^2) = 0.846, final $R1$ ($I > 2\sigma$) = 0.0376, $wR2$ ($I > 2\sigma$) = 0.0909, $R1$ (all data) = 0.0570, $wR2$ (all data) = 0.1042. For **2**: C$_{25}$H$_{18}$N$_3$NiS$_{10}$, $M_r = 739.73$, $a = 16.9262(13)$ Å, $b = 21.7766(17)$ Å, $c = 7.8174(6)$ Å, $V = 2881.5(4)$ Å^3, orthorhombic, space group *Pbcn*, $Z = 4$, $T = 297(2)$ K, $D_{\text{calcd}} = 1.705$ Mg m^{-3}, $\mu = 1.423$ mm^{-1}, 18147 reflections measured, 3329 unique ($R_{\text{int}} = 0.0817$), GOF (on F^2) = 0.999, final $R1$ ($I > 2\sigma$) = 0.0423, $wR2$ ($I > 2\sigma$) = 0.0836, $R1$ (all data) = 0.0832, $wR2$ (all data) = 0.0917. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-288075 and -288074 for compounds **1** and **2**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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