Crystal Structure of $Ni(dmit)_2$ Salts with Ammonium Ions Possessing Hydrogen-Bond Accepting Site

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Crystal structures of three $Ni(dmit)_2$ salts, whose counter cations ((2-methoxyethyl)ammonium, morpholinium, *N*-methylmorpholinium) consist of both hydrogen-bond donating and accepting sites, are reported. Within these salts, the $Ni(dmit)_2$ columns are structurally modulated by intermolecular hydrogen bonds between the $-NH^+$ group of the cation and the =S group of the dmit ligand. The alignment and the overlapping modes of $Ni(dmit)_2$ molecules are found to be mainly governed by the hydrogen bonding pattern.

Physical properties of molecular conductors depend on the molecular alignment in crystals. In crystals of highly conductive ion radical salts, donor or acceptor molecules are often aligned in a uniform columnar[1] or a herringbone[2] structure. Unfortunately prediction of the molecular alignment within crystals 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 is specific for functional groups, in other words, bonds are formed only between hydrogen donating (–OH, –NH etc.) and accepting sites (=O, –O– etc.) in a restricted geometry. The bonding schemes are therefore predictable to a certain extent.[3]

A $Ni(dmit)_2$ system (H_2dmit=4,5-dimercapto-1,3-dithiol-2-thione), for example, has an advantage in this viewpoint, since the dmit ligand has hydrogen bond accepting sites (=S groups). In this study we have adopted organic ions with both hydrogen donating and accepting sites, such as (2-methoxyethyl)ammonium (MEA), morpholinium (Hmorph) and *N*-methylmorpholinium (HMemorph) ions, as a counter ion of the $Ni(dmit)_2$ complex. Since all of these ions carry both a hydrogen donating site ($-NH^+$ group) and an accepting one (–O– group), there is a high possibility for these ions to form an intermolecular hydrogen-bonding scheme, in which $Ni(dmit)_2$ molecules may also be involved. In addition, variation from primary, secondary to tertiary ammonium ions will cause the difference in strength and geometry of hydrogen bonds, and the systematic change of cations may give information on the effect of hydrogen bonding both on the structure and transport properties of the conduction column.

From these points of view, we investigated the crystal structure and transport properties of three salts of the $Ni(dmit)_2$ complex, using the counter ion system mentioned above.

Experimental

Materials: *n*-$Bu_4N[Ni(dmit)_2]$ was prepared according to the literature.[4] $MEABPh_4$, $(Hmorph)BPh_4$, and $(HMemorph)BPh_4$ were obtained by mixing an aqueous solution of $NaBPh_4$ and an aqueous solution of hydrochloride of the corresponding amines. White precipitates were then recrystallized from a mixture of acetone and *n*-hexane (1 : 1, $MEABPh_4$), or acetone and water (1 : 1, the others).[5] Acetonitrile was dried over CaH_2 and distilled under a nitrogen atmosphere before use.

(MEA)$[Ni(dmit)_2]_3$·MeCN (1): Salts **1** were grown as black plates (typically 0.36×0.16×0.03 mm) by galvanostatic (I=1μA) oxidation of *n*-$Bu_4N[Ni(dmit)_2]$ (30 mg) in acetonitrile (20 ml), using $MEABPh_4$ (0.40 g) as a supporting electrolyte, and a platinum plate (10×5×0.5 mm) was used as an anode.

(Hmorph)$_2[Ni(dmit)_2]_3$ (2), (HMemorph)[Ni(dmit)$_2]_2$ (3): These salts were grown as black elongated plates (**2**: 0.55×0.18×0.04 mm, **3**: 0.60×0.15×0.03 mm) through a similar procedure as **1**, using $(Hmorph)BPh_4$ (0.41 g) and $(HMemorph)BPh_4$ (0.42 g) as a supporting electrolyte, respectively.

X-Ray Data Collection. Intensity data were collected at room temperature by a Rigaku AFC-5 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). Crystallographic data for **1**, **2**, and **3** are summarized in Table 1.[6] Calculations were performed on a FACOM A-70 computer.

(MEA)$[Ni(dmit)_2]_3$·MeCN (1): 6277 reflections ($4<2\theta<50°$) were collected using ω ($4<2\theta<40°$) and ω–2θ scan ($40\leq2\theta<50°$) methods, and 3477 independent reflections ($|F_o|>3\sigma(F_o)$) were used for the analysis. Absorption effect was corrected analytically[7] ($0.66<T<0.92$). The structure was solved by direct methods using SHELXS-86[8] and were refined by the block-diagonalized least-squares method using UNICS-III system[9] and ORTEP-II.[10] All of non-H atoms were refined anisotropically, and H atoms were fixed at the geometrically calculated positions. Final R=0.076, R_w=0.075, S=1.31, $w=(\sigma(F_o)^2+0.0006|F_o|^2)^{-1}$, max. (Δ/σ)=0.13, max. $(|\Delta\rho|)$=0.89 e Å^3.

(Hmorph)$_2[Ni(dmit)_2]_3$ (2): 4802 reflections ($4<2\theta<50°$) were measured using ω-scan method, and 2220 independent reflections ($|F_o|>3\sigma(F_o)$) were used for the analysis. Absorption effect was corrected analytically[7] ($0.79<T<0.99$). The structure was solved by direct methods using SAPI-85[11] and was refined by the block-diagonalized least-squares methods (UNICS-III). All of non-H atoms were refined anisotropically, and H atoms were fixed at the geo-

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Table 1. Crystallographic Data for the Salts

	MEA[Ni(dmit)$_2$]$_3$·MeCN (**1**)	(Hmorph)$_2$[Ni(dmit)$_2$]$_3$ (**2**)	HMemorph[Ni(dmit)$_2$]$_2$ (**3**)
Formula	$Ni_3S_{30}ON_2C_{23}H_{13}$	$Ni_3S_{30}O_2N_2C_{26}H_{20}$	$Ni_2S_{20}ONC_{17}H_{12}$
M	1472.10	1531.10	1005.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	11.917(2)	8.645(3)	11.602(3)
b/Å	11.097(2)	37.53(2)	19.905(6)
c/Å	37.692(9)	7.643(2)	7.558(4)
α/°	90	90	101.87(4)
β/°	105.62(2)	92.59(2)	99.09(4)
γ/°	90	90	76.35(2)
V/Å^3	4800(2)	2477(1)	1648(1)
Z	4	2	2
D_c/g cm^{-3}	2.037	2.053	2.025
$F(000)$	2948	1540	1010
μ(Mo $K\alpha$)/cm^{-1}	24.587	23.879	23.892

metrically calculated positions. Final R=0.057, R_w=0.059, S=3.48, w=0.4 ($|F_o|<40$), 1.0 ($40<|F_o|<100$), $10^4/|F_o|^2$ ($100<|F_o|$), max. (Δ/σ)=0.07, max. ($|\Delta\rho|$)=0.70 e Å^3.

(HMemorph)[Ni(dmit)$_2$]$_2$ (3): 8142 reflections ($4<2\theta<55°$) were measured using ω ($4<2\theta<40°$) and ω–2θ scan ($40<2\theta<55°$) methods, and 4733 independent reflections ($|F_o|>3\sigma(F_o)$) were used for the analysis. Absorption effect was corrected analytically[7] ($0.71<T<0.93$). The structure was solved by direct methods (SAPI-85) and were refined by the block-diagonalized least-squares method (UNICS-III). All of non-H atoms were refined anisotropically. H atoms were found on ΔF-map and refined isotropically. Final R=0.047, R_w=0.044, S=1.41, w=0.3 ($|F_o|<20$), 1.0 ($20<|F_o|<80$), $3000/|F_o|^2$ ($80<|F_o|$), max. (Δ/σ)=0.32, max. ($|\Delta\rho|$)=0.55 e Å^3.

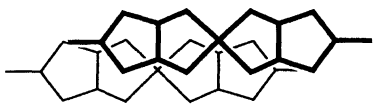
Electrical Conductivity: The DC electrical conductivity along the long axis of a crystal was measured with a four-probe method down to a liquid nitrogen temperature, using a handmade constant-current regulator (I=5—10 μA) and an ADVANTEST TR2114H digital multimeter. Electrical contacts to the sample were made by gold wire (25 μm) with gold paste (Tokuriki #8560).

Results and Discussion

Stoichiometry of the Salts. The ratio of Ni(dmit)$_2$ and counter ion is 1:3, 2:3, and 1:2 for the salts **1**, **2**, and **3**, respectively. Since the preparation procedure of these salts is practically the same and the cations show no redox behavior under these conditions (E<1.0 V vs. Ag/AgCl), this variation of the stoichiometry might simply be caused by the size and shape of the cation molecules. The existence of hydrogen bonding between cation molecules and dmit ligands also affect the composition of the crystals.

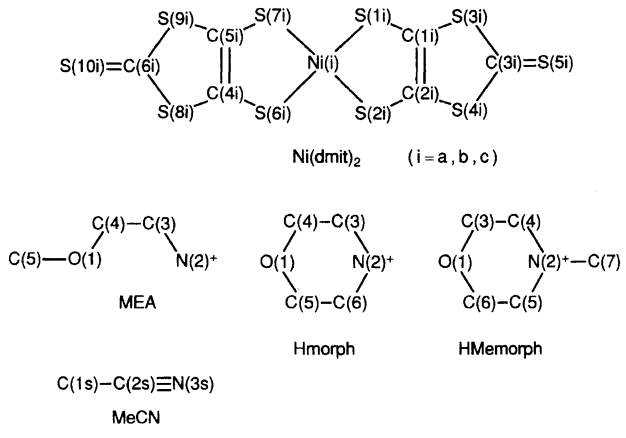
Overlapping Modes of Ni(dmit)$_2$ Molecules. On viewing crystal structures of various conductive Ni(dmit)$_2$ salts, it is recognized that there are two preferred overlapping modes of two Ni(dmit)$_2$ molecules, Types I and II (Fig. 1).[12] In Type I mode, a Ni(dmit)$_2$ molecule is located nearly above the other to have a tight ovelapping between them. For Type II mode, however, a Ni(dmit)$_2$ molecule is "slipped" about 3 Å along the long axis of the a molecule below. The overlapping between them is therefore weaker than that of Type I. The tendency can be semiquantitatively illustrated by comparing overlap integrals between LUMOs of two Ni(dmit)$_2$ molecules in these two modes (Type I: -26×10^{-3}, Type II: 4×10^{-3}; Interplanar distance ca.

Type I



Type II

Fig. 1. Two overlapping modes of Ni(dmit)$_2$ molecules.



Scheme 1.

Table 2. Atomic Parameters, Selected Bond Lengths (Å), and Angles (°) of **1**, with esd's in Parentheses

Atom	x	y	z	B_{eq}[a)]
Ni(dmit)$_2$				
Molecule A				
Ni(a)	0.2526(2)	0.4959(2)	0.2077(1)	1.9(1)
S(1a)	0.2033(3)	0.3664(4)	0.1634(1)	2.3(1)
S(2a)	0.2969(4)	0.6307(4)	0.1723(1)	2.9(1)
S(3a)	0.2117(4)	0.3754(4)	0.0843(1)	3.0(1)
S(4a)	0.2951(4)	0.6221(4)	0.0922(1)	3.0(1)
S(5a)	0.2567(4)	0.5021(5)	0.0199(1)	4.1(1)
S(6a)	0.3027(4)	0.6258(4)	0.2513(1)	2.6(1)
S(7a)	0.2034(4)	0.3647(3)	0.2424(1)	2.4(1)
S(8a)	0.3053(3)	0.6136(4)	0.3318(1)	2.3(1)
S(9a)	0.2046(4)	0.3728(4)	0.3228(1)	2.9(1)
S(10a)	0.2554(5)	0.4926(6)	0.3955(1)	4.8(2)
C(1a)	0.2339(12)	0.4379(13)	0.1279(3)	1.5(4)
C(2a)	0.2729(12)	0.5551(15)	0.1309(4)	2.3(4)
C(3a)	0.2541(13)	0.5001(16)	0.0627(4)	2.6(4)
C(4a)	0.2791(12)	0.5507(13)	0.2881(4)	1.8(4)
C(5a)	0.2300(12)	0.4364(13)	0.2838(4)	1.8(4)
C(6a)	0.2552(12)	0.4972(16)	0.3528(4)	2.5(4)
Molecule B				
Ni(b)	0.5830(2)	0.4943(2)	0.2355(1)	1.9(1)
S(1b)	0.5363(4)	0.3635(4)	0.1904(1)	2.8(1)
S(2b)	0.6326(3)	0.6305(3)	0.2017(1)	2.0(1)
S(3b)	0.5344(4)	0.3886(4)	0.1101(1)	2.3(1)
S(4b)	0.6339(4)	0.6290(4)	0.1212(1)	2.5(1)
S(5b)	0.5784(4)	0.5207(4)	0.0466(1)	3.8(2)
S(6b)	0.6354(4)	0.6202(3)	0.2806(1)	2.1(1)
S(7b)	0.5270(4)	0.3622(4)	0.2691(1)	2.4(1)
S(8b)	0.6325(4)	0.6036(4)	0.3601(1)	3.1(1)
S(9b)	0.5333(4)	0.3630(4)	0.3496(1)	2.6(1)
S(10b)	0.5918(5)	0.4681(5)	0.4243(1)	4.3(2)
C(1b)	0.5595(14)	0.4457(15)	0.1540(4)	2.9(5)
C(2b)	0.6037(15)	0.5596(17)	0.1594(5)	1.7(5)
C(3b)	0.5786(14)	0.5113(17)	0.0901(5)	3.3(5)
C(4b)	0.6035(11)	0.5447(12)	0.3154(4)	1.5(4)
C(5b)	0.5552(12)	0.4303(13)	0.3109(4)	1.7(4)
C(6b)	0.5836(14)	0.4775(13)	0.3798(4)	2.3(4)
Molecule C				
Ni(c)	0.9617(2)	0.4953(2)	0.2642(1)	2.1(1)
S(1c)	0.8575(3)	0.3646(3)	0.2211(1)	2.0(1)
S(2c)	0.9678(4)	0.6209(4)	0.2275(1)	3.0(1)
S(3c)	0.8589(4)	0.3618(4)	0.1417(1)	3.2(1)
S(4c)	0.9620(4)	0.6023(4)	0.1473(1)	3.0(1)
S(5c)	0.9085(5)	0.4706(5)	0.0755(1)	4.7(2)
S(6c)	0.9682(4)	0.6315(4)	0.3060(1)	2.9(1)
S(7c)	0.8379(3)	0.3680(4)	0.3014(1)	2.4(1)
S(8c)	0.9700(4)	0.6298(4)	0.3868(1)	2.5(1)
S(9c)	0.8820(4)	0.3849(4)	0.3822(1)	3.0(1)
S(10c)	0.9168(5)	0.5236(5)	0.4517(1)	4.4(2)
C(1c)	0.9369(13)	0.5473(14)	0.1872(5)	2.5(5)
C(2c)	0.8884(12)	0.4323(14)	0.1847(4)	2.0(4)
C(3c)	0.9122(14)	0.4812(17)	0.1189(4)	3.2(5)
C(4c)	0.9478(15)	0.5638(15)	0.3441(5)	3.2(6)
C(5c)	0.9084(13)	0.4441(13)	0.3422(4)	2.1(5)
C(6c)	0.9253(13)	0.5127(17)	0.4094(4)	2.9(5)
MEA				
O(1d)	0.3708(10)	0.9017(10)	−0.0136(3)	3.4(4)
N(2d)	0.5921(14)	0.8237(15)	0.0275(4)	4.6(6)
C(3d)	0.5432(18)	0.7997(18)	−0.0127(6)	5.0(8)
C(4d)	0.4130(16)	0.7889(18)	−0.0208(5)	3.9(6)
C(5d)	0.2503(17)	0.8904(19)	−0.0176(5)	4.8(7)
MeCN				
C(1s)	0.0077(18)	0.7026(20)	0.0167(6)	5.6(8)
C(2s)	−0.0918(18)	0.7566(20)	0.0251(6)	5.3(8)
N(3s)	−0.1707(16)	0.7945(17)	0.0333(7)	7.8(9)

a) $B_{eq}=4/3(\beta_{11}\boldsymbol{a}\cdot\boldsymbol{a}+\beta_{12}\boldsymbol{a}\cdot\boldsymbol{b}+\cdots)$.

	Molecule A	B	C
Ni(dmit)$_2$			
Ni–S(1)	2.161(5)	2.190(5)	2.151(5)
Ni–S(2)	2.161(5)	2.160(5)	2.166(5)
Ni–S(6)	2.147(5)	2.160(5)	2.149(5)
Ni–S(7)	2.141(5)	2.157(5)	2.144(5)
S(1)–C(1)	1.679(15)	1.730(18)	1.691(16)
S(2)–C(2)	1.727(17)	1.726(16)	1.675(18)
S(3)–C(1)	1.740(15)	1.721(17)	1.748(16)
S(3)–C(3)	1.748(19)	1.708(19)	1.785(19)
S(4)–C(2)	1.723(17)	1.774(16)	1.723(18)
S(4)–C(3)	1.736(19)	1.761(19)	1.720(19)
S(5)–C(3)	1.623(19)	1.642(20)	1.630(20)
S(6)–C(4)	1.703(16)	1.684(15)	1.696(19)
S(7)–C(5)	1.707(15)	1.699(15)	1.705(17)
S(8)–C(4)	1.740(16)	1.753(16)	1.725(19)
S(8)–C(6)	1.705(19)	1.754(17)	1.715(19)
S(9)–C(5)	1.728(16)	1.722(15)	1.750(17)
S(9)–C(6)	1.784(19)	1.703(17)	1.746(19)
S(10)–C(6)	1.608(19)	1.659(17)	1.628(20)
C(1)–C(2)	1.376(22)	1.343(23)	1.394(23)
C(4)–C(5)	0.387(21)	1.385(21)	1.404(24)
S(1)–Ni–S(2)	92.6(2)	93.4(2)	92.4(2)
S(1)–Ni–S(6)	179.3(2)	177.9(2)	177.1(2)
S(1)–Ni–S(7)	87.5(2)	87.2(2)	87.8(2)
S(2)–Ni–S(6)	86.2(2)	86.9(2)	86.6(2)
S(2)–Ni–S(7)	178.2(2)	177.7(2)	1077.5(2)
S(6)–Ni–S(7)	93.1(2)	92.7(2)	93.3(2)
Ni–S(1)–C(1)	103.2(5)	101.8(6)	102.4(6)
Ni–S(1)–C(2)	102.3(6)	101.1(5)	103.6(6)
C(1)–S(3)–C(3)	97.8(8)	97.9(9)	96.0(8)
C(2)–S(4)–C(3)	97.2(8)	95.3(8)	98.8(9)
Ni–S(6)–C(4)	102.8(5)	102.3(5)	103.3(7)
Ni–S(7)–C(5)	103.2(5)	103.1(5)	102.7(6)
C(4)–S(8)–C(6)	98.0(8)	96.1(8)	98.7(9)
C(5)–S(9)–C(6)	96.6(8)	97.7(8)	96.3(8)
S(1)–C(1)–S(3)	123.8(9)	123.0(10)	124.8(11)
S(1)–C(1)–C(2)	121.5(12)	120.0(13)	119.6(13)
S(3)–C(1)–C(2)	114.6(11)	117.0(13)	115.6(13)
S(2)–C(2)–S(4)	122.1(10)	120.3(9)	121.4(9)
S(2)–C(2)–C(1)	120.2(12)	123.6(13)	121.9(13)
S(4)–C(2)–C(1)	117.7(12)	116.1(12)	116.7(12)
S(3)–C(3)–S(4)	112.8(10)	113.6(11)	112.9(10)
S(3)–C(3)–S(5)	124.0(11)	125.1(12)	120.8(11)
S(4)–C(3)–S(5)	123.3(11)	121.2(11)	126.3(12)
S(6)–C(4)–S(8)	129.2(9)	122.4(9)	125.6(11)
S(6)–C(4)–C(5)	120.7(12)	122.3(12)	119.8(14)
S(8)–C(4)–C(5)	116.0(11)	115.3(11)	114.6(13)
S(7)–C(5)–S(9)	123.8(9)	123.8(9)	122.4(10)
S(7)–C(5)–C(4)	120.0(12)	119.6(11)	120.8(13)
S(9)–C(5)–C(4)	116.2(11)	116.5(11)	116.4(13)
S(8)–C(6)–S(9)	113.2(10)	114.3(9)	113.9(11)
S(8)–C(6)–S(10)	125.5(12)	122.8(10)	122.6(12)
S(9)–C(6)–S(10)	121.3(11)	122.8(10)	123.4(12)
MEA			
O(1)–C(4)	1.404(23)		
O(1)–C(5)	1.407(24)		
N(2)–C(3)	1.494(27)		
C(3)–C(4)	1.503(29)		
C(4)–O(1)–C(5)	107.9(14)		
O(1)–C(4)–C(3)	107.1(16)		
N(2)–C(3)–C(4)	108.7(17)		
MeCN			
C(1)–C(2)	1.437(33)		
C(2)–N(3)	1.146(34)		
C(1)–C(2)–N(3)	175.9(26)		

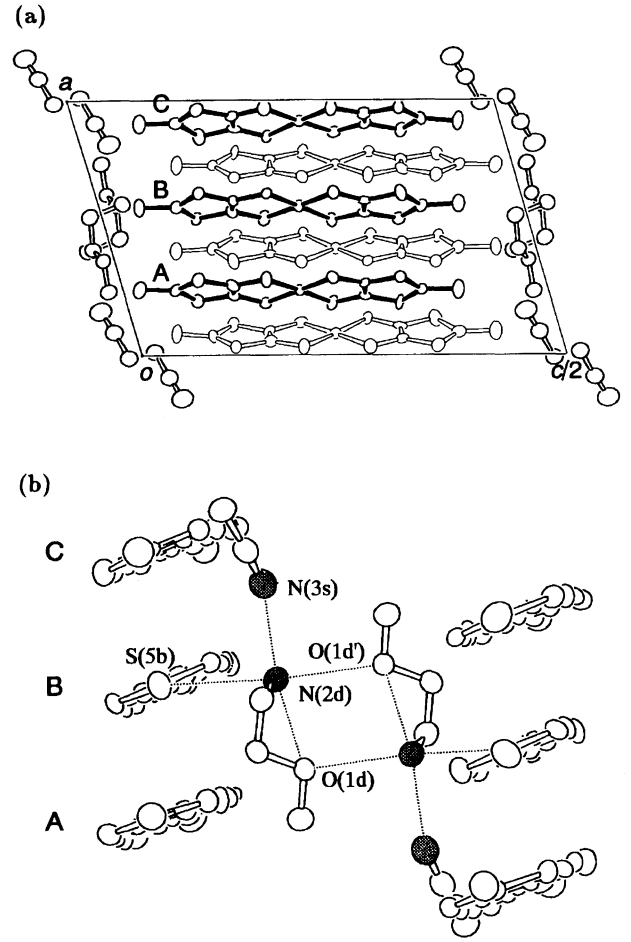


Fig. 2. a) Crystal structure of (MEA)[Ni(dmit)$_2$]$_3$·MeCN. Ni(dmit)$_2$ molecules with filled bonds are stacked within a column at $y\approx1/2$, while the others are located around $y\approx0$. b) Hydrogen bonding scheme of the salt. Shaded ellipsoids represent nitrogen atoms.

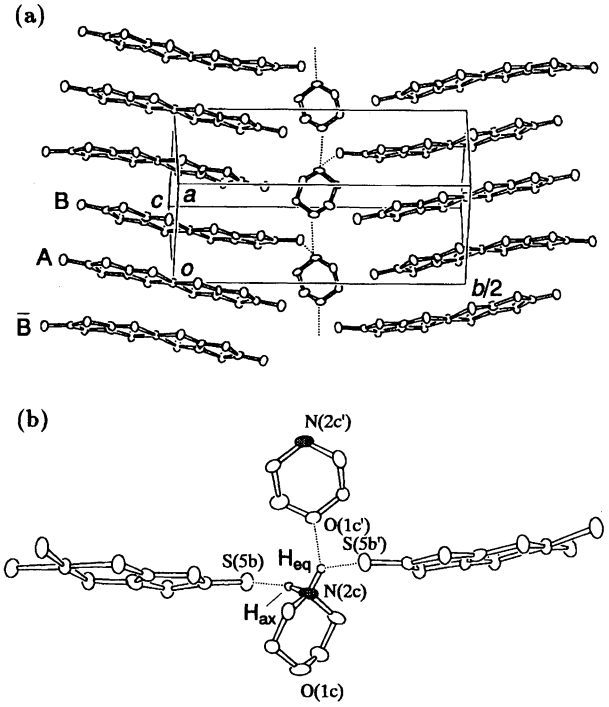


Fig. 3. a) Crystal structure of (Hmorph)$_2$[Ni(dmit)$_2$]$_3$. b) Hydrogen bonding scheme of the salt. Shaded ellipsoids represent nitrogen atoms.

3.55 Å).[12] In the case of a metallic TTF[Ni(dmit)$_2$]$_2$ salt, for example, the Ni(dmit)$_2$ column is uniform, and every overlapping is classified as Type I.[1] On the other hand, a semiconductive TSF[Ni(dmit)$_2$]$_3$ salt has the conduction column of trimeric structure, i.e. the overlapping sequence is -I-I-II-I-I-II-.[13] Considering the strong one-dimensionality of the Ni(dmit)$_2$ column,[12] the difference in the overlapping periodicity might cause the variation in transport properties of the salts. Overlapping modes of Ni(dmit)$_2$ columns of the obtained salts will be discussed from this viewpoint (Scheme 1).

(MEA)[Ni(dmit)$_2$]$_3$·MeCN (1): Atomic parameters, selected bond lengths and angles are given in Table 2. Figure 2a shows half of the unit cell viewed along the *b*-axis. There are three crystallographically independent Ni(dmit)$_2$ molecules (A, B, and C) within an asymmetric unit, and no significant difference in their bond lengths and angles are recognized. Maximum deviations from least-squares planes for molecules A, B, and C are 0.071(5) [S(2a)], 0.091(6) [S(10b)], and 0.123 (6) Å [S(10c)], respectively. These three molecules are stacked in the order of ···C–B–A–C–B··· to form a column, which is elongated parallel to the *a*-axis. The overlapping modes of adjacent Ni(dmit)$_2$ molecules are classified as Type I for A-B, B-C pairs, and Type II for C-A, and the overlapping sequence is therefore described as -I-I-II-I-I-II-. The separations between molecular planes are 3.518(4), 3.546(4), and 3.590(4) Å for A-B, B-C, and C-A pairs, respectively. There are many intercolumnar side-by-side S···S contacts (minimum: 3.491(7) Å [S(7a)–S(6c)]), whose distances are shorter than the twice of Bondi's van der Waals radius of sulfur atom (3.70 Å).[14] As for the MEA cation, bond lengths and angles are within a normal range, and conformation around C(4d)–O(1d) and C(3d)–C(4d) bonds are *trans* and *gauche*, respectively (torsional angles: C(5d)–O(1d)–C(4d)–C(3d): −174(2), N(2d)–C(3d)–C(4d)–O(1d): 64(2)°). Two cations make a dimer through both intra- and intermolecular hydrogen bonds, and two acetonitrile molecules are also incorporated within this unit (Fig. 2b). Applying MM2 force field,[15] the difference in the steric energy between *trans–gauche* and *trans–trans* conformers is at most 3.4 kJ mol^{-1} and is easily compensated by the formation of these hydrogen bonds. As a result, MEA cations do not form a one-dimentional chain but a head-to-tail dimer. The Ni(dmit)$_2$ molecules typed as B are also hydrogen-bonded to this cation unit. Thus each $-NH_3^+$ group is surrounded by four atoms (N(2d)···O(1d): 2.81(2) (intramolecular), 3.14(2) (intermolecular), N(2d)··· N(3s): 2.80(3), N(2d)···S(5b): 3.45(2) Å), and at

Table 3. Atomic Parameters, Selected Bond Lengths (Å), and Angles (°) of **2**, with esd's in Parentheses

Atom	x	y	z	B_{eq}
$Ni(dmit)_2$				
Molecule A[a)]				
Ni(a)	0.	0.	0.	2.2(1)
S(1a)	−0.1107(4)	−0.0406(1)	0.1527(4)	3.0(1)
S(2a)	0.1742(3)	−0.0368(1)	−0.0891(4)	2.7(1)
S(3a)	−0.0507(4)	−0.1194(1)	0.1887(5)	3.1(1)
S(4a)	0.2162(4)	−0.1157(1)	−0.0240(4)	3.1(1)
S(5a)	0.1295(4)	−0.1857(1)	0.1270(5)	3.8(1)
C(1a)	−0.0075(12)	−0.0778(3)	0.1069(14)	1.8(3)
C(2a)	0.1211(14)	−0.0755(3)	0.0061(16)	2.6(3)
C(3a)	0.1008(14)	−0.1424(3)	0.0980(16)	2.7(3)
Molecule B				
Ni(b)	0.3050(2)	0.0280(1)	0.2958(2)	2.2(1)
S(1b)	0.4306(3)	0.0675(1)	0.1494(4)	2.6(1)
S(2b)	0.1423(3)	0.0668(1)	0.3947(4)	2.4(1)
S(3b)	0.3864(4)	0.1474(1)	0.1230(4)	2.5(1)
S(4b)	0.1307(3)	0.1468(1)	0.3484(4)	2.5(1)
S(5b)	0.2549(4)	0.2167(1)	0.2424(4)	2.6(1)
S(6b)	0.4755(4)	−0.0100(1)	0.2158(4)	2.9(1)
S(7b)	0.1829(3)	−0.0118(1)	0.4413(4)	2.7(1)
S(8b)	0.5251(3)	−0.0873(1)	0.3059(4)	2.6(1)
S(9b)	0.2512(3)	−0.0896(1)	0.5090(4)	2.6(1)
S(10b)	0.4316(4)	−0.1558(1)	0.4629(5)	3.4(1)
C(1b)	0.3315(14)	0.1053(3)	0.1964(15)	2.7(3)
C(2b)	0.2076(13)	0.1052(3)	0.3017(15)	2.5(3)
C(3b)	0.2579(13)	0.1722(3)	0.2296(15)	1.9(3)
C(4b)	0.4222(12)	−0.0472(3)	0.3198(15)	2.5(3)
C(5b)	0.2197(12)	−0.0484(3)	0.4182(15)	2.2(3)
C(6b)	0.4056(12)	−0.1132(3)	0.4276(14)	2.3(3)
Hmorph				
O(1c)	0.1894(10)	0.2434(2)	0.6643(10)	3.2(2)
N(2c)	0.4369(11)	0.2521(3)	0.9186(12)	2.7(3)
C(3c)	0.4387(13)	0.2235(3)	0.7816(16)	2.5(3)
C(4c)	0.2710(14)	0.2131(3)	0.7320(17)	2.7(3)
C(5c)	0.1815(15)	0.2707(4)	0.7915(18)	3.6(4)
C(6c)	0.3439(13)	0.2832(3)	0.8538(16)	2.8(3)

a) Since molecule A lies on the inversion center, atomic parameters of half of the molecule are listed.

		Molecule A	B
$Ni(dmit)_2$	Ni–S(1)	2.168(3)	2.175(4)
	Ni–S(2)	2.175(3)	2.182(3)
	Ni–S(6)		2.160(4)
	Ni–S(7)		2.166(3)
	S(1)–C(1)	1.703(11)	1.705(12)
	S(2)–C(2)	1.698(12)	1.715(12)
	S(3)–C(1)	1.729(11)	1.748(12)
	S(3)–C(3)	1.739(13)	1.688(12)
	S(4)–C(2)	1.738(12)	1.740(12)
	S(4)–C(3)	1.718(12)	1.742(12)
	S(5)–C(3)	1.657(13)	1.674(12)
	S(6)–C(4)		1.680(12)
	S(7)–C(5)		1.677(12)
	S(8)–C(4)		1.756(12)
	S(8)–C(6)		1.721(12)
	S(9)–C(5)		1.738(12)
	S(9)–C(6)		1.739(12)
	S(10)–C(6)		1.636(12)
	C(1)–C(2)	1.384(16)	1.368(17)
	C(4)–C(5)		1.385(16)
	S(1)–Ni–S(2)	92.9(1)	94.0(1)
	S(1)–Ni–S(6)		86.6(1)
	S(1)–Ni–S(7)		179.1(1)
	S(2)–Ni–S(6)		175.9(1)
	S(2)–Ni–S(7)		86.8(1)
	S(6)–Ni–S(7)		92.5(1)
	Ni–S(1)–C(1)	102.6(4)	101.0(4)
	Ni–S(2)–C(2)	101.8(4)	100.8(4)
	C(1)–S(3)–C(3)	97.2(6)	98.6(6)
	C(2)–S(4)–C(3)	98.3(6)	97.4(6)
	Ni–S(6)–C(4)		102.1(4)
	Ni–S(7)–C(5)		102.8(4)
	C(4)–S(8)–C(6)		97.6(6)
	C(5)–S(9)–C(6)		98.0(5)
	S(1)–C(1)–S(3)	122.9(6)	122.6(7)
	S(1)–C(1)–C(2)	120.4(9)	122.3(9)
	S(3)–C(1)–C(2)	116.7(8)	115.0(9)
	S(2)–C(2)–S(4)	123.2(7)	122.2(7)
	S(2)–C(2)–C(1)	122.1(9)	121.9(9)
	S(4)–C(2)–C(1)	114.6(9)	115.7(9)
	S(3)–C(3)–S(4)	113.1(7)	113.2(6)
	S(3)–C(3)–S(5)	123.0(7)	126.3(7)
	S(4)–C(3)–S(5)	123.9(7)	120.3(7)
	S(6)–C(4)–S(8)		122.2(7)
	S(6)–C(4)–C(5)		122.1(9)
	S(8)–C(4)–C(5)		115.6(9)
	S(7)–C(5)–S(9)		124.2(7)
	S(7)–C(5)–C(4)		120.3(9)
	S(9)–C(5)–C(4)		115.4(9)
	S(8)–C(6)–S(9)		113.3(6)
	S(8)–C(6)–S(10)		124.0(7)
	S(9)–C(6)–S(10)		122.7(7)
Hmorph	O(1)–C(4)	1.425(15)	
	O(1)–C(5)	1.415(16)	
	N(2)–C(3)	1.502(16)	
	N(2)–C(6)	1.487(16)	
	C(3)–C(4)	1.533(18)	
	C(5)–C(6)	1.535(19)	
	C(4)–O(1)–C(5)	111.6(9)	
	C(3)–N(2)–C(6)	110.5(9)	
	N(2)–C(3)–C(4)	108.4(10)	
	O(1)–C(4)–C(3)	109.5(10)	
	O(1)–C(5)–C(6)	111.2(11)	
	N(2)–C(6)–C(5)	109.8(10)	

least one of three ammonium hydrogen atoms participates a three-centered bifurcated hydrogen bond. Considering the statistical mean values for each type of hydrogen bond (N···O: 2.89(11), N···N: 2.98(16), N···S: 3.42(11) Å),[16] the strength of these bonds is moderate or weak. Through these hydrogen bonds, the neighboring trimeric $Ni(dmit)_2$ units are connected via the cationic dimer. Existence of the hydrogen bond to the anion column may cause charge localization within the column, based on the electrostatic factor in the hydrogen bond. In general, the amount of the negative charge on $Ni(dmit)_2$ molecule can be estimated by Ni–S bond length, i.e. the bond length becomes longer as the negative charge increases ($[Ni(dmit)_2]^0$: 2.147(2), $[Ni(dmit)_2]^{-1}$: 2.156(3), $[Ni(dmit)_2]^{-2}$: 2.216(6) Å).[17] As for the salt **1**, no significant difference in the Ni–S distance among molecules A, B, and C is observed as mentioned before. Therefore the charge localization on the $Ni(dmit)_2$ column

Table 4. Atomic Parameters, Selected Bond Lengths (Å), and Angles (°) of **3**, with esd's in Parentheses

	Atom	x	y	z	B_{eq}
Ni(dmit)$_2$ Molecule A					
	Ni(a)	0.3621(1)	0.5025(1)	0.1121(1)	2.25(2)
	S(1a)	0.2260(1)	0.5801(1)	−0.0062(2)	2.86(4)
	S(2a)	0.4522(1)	0.5805(1)	0.2812(2)	2.68(4)
	S(3a)	0.1867(1)	0.7385(1)	0.0549(2)	2.88(4)
	S(4a)	0.3933(1)	0.7392(1)	0.3261(2)	2.89(4)
	S(5a)	0.2513(2)	0.8742(1)	0.2288(2)	3.52(5)
	S(6a)	0.2665(1)	0.4272(1)	−0.0563(2)	2.77(4)
	S(7a)	0.4983(1)	0.4219(1)	0.2233(2)	2.73(4)
	S(8a)	0.3194(1)	0.2692(1)	−0.1181(2)	2.78(4)
	S(9a)	0.5319(1)	0.2635(1)	0.1420(2)	2.99(5)
	S(10a)	0.4643(2)	0.1307(1)	−0.0579(3)	3.99(6)
	C(1a)	0.2665(5)	0.6577(3)	0.0996(8)	2.4(2)
	C(2a)	0.3650(5)	0.6572(3)	0.2260(8)	2.4(2)
	C(3a)	0.2752(5)	0.7877(3)	0.2046(8)	2.4(2)
	C(4a)	0.3536(5)	0.3493(3)	−0.0126(7)	2.3(2)
	C(5a)	0.4552(5)	0.3463(3)	0.1102(8)	2.2(2)
	C(6a)	0.4395(5)	0.2169(3)	−0.0122(8)	2.7(2)
Molecule B	Ni(b)	0.1657(1)	0.4153(1)	0.3570(1)	2.15(2)
	S(1b)	0.3039(1)	0.3370(1)	0.4786(2)	2.68(4)
	S(2b)	0.0771(1)	0.3345(1)	0.1863(2)	2.74(4)
	S(3b)	0.3454(1)	0.1778(1)	0.4139(2)	2.97(4)
	S(4b)	0.1451(1)	0.1762(1)	0.1370(2)	3.13(5)
	S(5b)	0.2989(2)	0.0400(1)	0.2150(2)	3.25(5)
	S(6b)	0.2554(1)	0.4925(1)	0.5194(2)	2.78(4)
	S(7b)	0.0261(1)	0.4903(1)	0.2421(2)	2.82(4)
	S(8b)	0.1931(1)	0.6509(1)	0.5674(2)	3.08(5)
	S(9b)	−0.0185(1)	0.6488(1)	0.3069(2)	3.17(5)
	S(10b)	0.0400(2)	0.7855(1)	0.4864(3)	4.61(6)
	C(1b)	0.2642(5)	0.2600(3)	0.3718(7)	2.3(2)
	C(2b)	0.1678(5)	0.2587(3)	0.2428(8)	2.6(2)
	C(3b)	0.2644(5)	0.1280(3)	0.2520(8)	2.6(2)
	C(4b)	0.1650(5)	0.5688(3)	0.4693(8)	2.4(2)
	C(5b)	0.0632(5)	0.5677(3)	0.3456(8)	2.3(2)
	C(6b)	0.0700(5)	0.7000(3)	0.4546(8)	2.9(2)
HMemorph	O(1c)	0.9842(3)	0.0146(2)	0.2857(6)	4.0(2)
	N(2c)	0.7354(4)	0.0141(3)	0.2426(6)	2.9(2)
	C(3c)	0.9015(6)	0.0596(4)	0.1802(9)	3.8(2)
	C(4c)	0.7799(6)	0.0797(3)	0.2464(9)	3.7(2)
	C(5c)	0.8265(5)	−0.0363(3)	0.3404(9)	3.4(2)
	C(6c)	0.9446(6)	−0.0487(4)	0.2713(9)	4.0(2)
	C(7c)	0.6178(6)	0.0305(4)	0.3154(9)	4.1(2)

		Molecule A	B
Ni(dmit)$_2$	Ni–S(1)	2.156(2)	2.166(2)
	Ni–S(2)	2.160(2)	2.169(2)
	Ni–S(6)	2.156(2)	2.154(2)
	Ni–S(7)	2.171(2)	2.156(2)
	S(1)–C(1)	1.721(6)	1.709(6)
	S(2)–C(2)	1.711(6)	1.714(6)
	S(3)–C(1)	1.725(6)	1.748(6)
	S(3)–C(3)	1.716(6)	1.715(6)
	S(4)–C(2)	1.734(6)	1.733(6)
	S(4)–C(3)	1.731(6)	1.710(6)
	S(5)–C(3)	1.655(6)	1.677(6)
	S(6)–C(4)	1.704(6)	1.705(6)
	S(7)–C(5)	1.713(6)	1.696(6)
	S(8)–C(4)	1.734(6)	1.732(6)
	S(8)–C(6)	1.723(6)	1.739(7)
	S(9)–C(5)	1.725(6)	1.725(6)
	S(9)–C(6)	1.730(6)	1.733(7)
	S(10)–C(6)	1.644(6)	1.629(7)
	C(1)–C(2)	1.369(8)	1.364(8)
	C(4)–C(5)	1.377(8)	1.387(8)
	S(1)–Ni–S(2)	93.0(1)	93.6(1)
	S(1)–Ni–S(6)	85.3(1)	87.0(1)
	S(1)–Ni–S(7)	178.2(1)	178.6(1)
	S(2)–Ni–S(6)	178.0(1)	178.3(1)
	S(2)–Ni–S(7)	88.6(1)	86.7(1)
	S(6)–Ni–S(7)	93.1(1)	92.7(1)
	Ni–S(1)–C(1)	102.8(2)	101.7(2)
	Ni–S(2)–C(2)	102.4(2)	101.4(2)
	C(1)–S(3)–C(3)	96.5(3)	97.1(3)
	C(2)–S(4)–C(3)	96.6(3)	97.5(3)
	Ni–S(6)–C(4)	102.4(2)	102.9(2)
	Ni–S(7)–C(5)	102.3(2)	103.1(2)
	C(4)–S(8)–C(6)	96.9(3)	97.1(3)
	C(5)–S(9)–C(6)	97.1(3)	98.0(3)
	S(1)–C(1)–S(3)	122.7(4)	123.0(3)
	S(1)–C(1)–C(2)	120.2(5)	121.6(5)
	S(3)–C(1)–C(2)	117.1(5)	115.4(4)
	S(2)–C(2)–S(4)	123.0(4)	122.4(4)
	S(2)–C(2)–C(1)	121.7(5)	121.6(5)
	S(4)–C(2)–C(1)	115.3(5)	115.9(5)
	S(3)–C(3)–S(4)	114.4(3)	114.0(3)
	S(3)–C(3)–S(5)	123.0(4)	122.3(4)
	S(4)–C(3)–S(5)	122.6(4)	123.7(4)
	S(6)–C(4)–S(8)	122.2(3)	122.9(3)
	S(6)–C(4)–C(5)	121.7(4)	120.7(5)
	S(8)–C(4)–C(5)	116.1(4)	116.4(4)
	S(7)–C(5)–S(9)	123.5(3)	124.0(4)
	S(7)–C(5)–C(4)	120.5(4)	120.6(5)
	S(9)–C(5)–C(4)	115.9(4)	115.4(4)
	S(8)–C(6)–S(9)	113.9(3)	113.1(4)
	S(8)–C(6)–S(10)	122.5(4)	123.4(4)
	S(9)–C(6)–S(10)	123.6(4)	123.5(4)
HMemorph	O(1)–C(3)	1.415(9)	
	O(1)–C(6)	1.420(9)	
	N(2)–C(4)	1.507(9)	
	N(2)–C(5)	1.493(9)	
	N(2)–C(7)	1.491(9)	
	C(3)–C(4)	1.508(10)	
	C(5)–C(6)	1.491(10)	
	C(3)–O(1)–C(6)	109.5(5)	
	C(4)–N(2)–C(5)	110.8(5)	
	C(4)–N(2)–C(7)	111.8(5)	
	C(5)–N(2)–C(7)	111.8(5)	
	O(1)–C(3)–C(4)	111.9(6)	
	N(2)–C(4)–C(3)	109.2(6)	
	N(2)–C(4)–C(6)	110.6(6)	
	O(1)–C(6)–C(5)	112.1(6)	

may not be substantial.

(Hmorph)$_2$[Ni(dmit)$_2$]$_3$ (2): Atomic parameters, selected bond lengths and angles are given in Table 3. Figure 3a shows half of the unit cell. There are two crystallographically independent Ni(dmit)$_2$ molecules (A and B) within an asymmetric unit. Molecule A lies on the inversion center and approximately planar (max. deviation from least-squares plane: 0.073(6) Å [S(3a)]), while molecule B shows a considerable deviation from planarity. Coordination of NiS_4 is slightly twisted (the dihedral angle between two Ni(S_2C_2) moieties: 5.8(2)°), and one of the 1,3-dithiol ring also shows a puckering (the dihedral angle between Ni(S_2C_2) and CS_3 moieties: 7.2(2)°), while the other ligand is almost planar (max. deviation from Ni(S_5C_3) plane: 0.045(3) Å [S(6b)]). The similar V-shaped distortion is observed in some M(dmit)$_2$ (M=Pd, Pt) salts,[18] but their origin is ascribed to the metal–metal

Table 5. Summary of Structural Properties of the Obtained Salts

$Ni(dmit)_2$ salt: cation (abbrev.) in parentheses	**1** (MEA)	**2** (Hmorph)	**3** (HMemorph)
Stoichiometry of cation and anion	1 : 3	2 : 3	1 : 2
Overlapping modes within $Ni(dmit)_2$ column (= : Type I, − : Type II)	=C–A=B=C–A=	=B–B=A=B–B=	–B–B–A=A–B–B–
H-Bond scheme of counter ion system	Dimeric clustur including solvent	One-dimentional H-bonded chain	Isolated

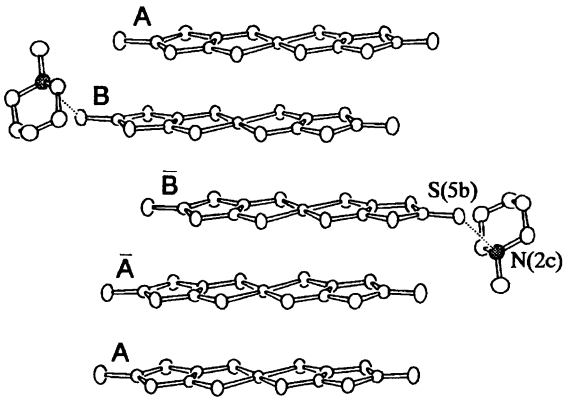


Fig. 4. Hydrogen bonding scheme of (HMemorph)-$[Ni(dmit)_2]_2$. Shaded ellipsoids represent nitrogen atoms.

interaction, which does not apparently exist in the case of Ni complexes. Thus the origin of the deviation in the salt **2** may be ascribed mainly to the steric effect as in the case of some $Ni(dmit)_2$ salts.[19] In this salt **2**, three molecules (B–A–$\overline{B}$, $\overline{B}$ is related to B by inversion) construct a "trimeric" unit, within a one-dimensional columnar structure along the $a+c$ direction. The overlapping mode between molecules A and B belongs to Type I, while the mode between B and $\overline{B}$ is Type II. The overlapping sequence is therefore described as -I-I-II-I-I-II-. The separations between molecular planes are 3.443(3) and 3.753(3) Å for A–B and B–$\overline{B}$ pairs, respectively. The latter is larger than usual, which is due to the nonplanarity of the molecule B. Morpholinium cations have a chair-type conformation and are aligned in the same direction. The hydrogen bonding pattern can be described as follows (Fig. 3b): The axial hydrogen on N(2c) (H_{ax}) forms a hydrogen bond to the thiocarbonyl group of molecule B (N(2c)···S(5b): 3.29(1) Å). The equatorial hydrogen atom (H_{eq}) lies on the O–N–S plane and constructs a bifurcated hydrogen bond (N(2c)···O(1c): 2.82(1) Å, N(2c)···S(5b): 3.32(1) Å). These N···S lengths are shorter than usual (3.42(11) Å).[16] As a result, the one-dimensional chain of cations ties the neighboring $Ni(dmit)_2$ column to construct a two-dimensional network through the hydrogen bonds. These relatively strong intermolecular hydrogen bonds between the cation and the thiocarbonyl group also play a role in the distortion of the molecule B in the anion column.

Since no significant difference in Ni–S distances is recognized between the hydrogen-bonded dmit ligand of molecule B (2.179(4) Å) and the other ligands (2.169-(3) Å), charge localization within the B–A–$\overline{B}$ trimeric unit is small, despite the large structural perturbation caused by the hydrogen bond. The result of extended Hückel MO calculations[12] shows that the negative charge on the thiocarbonyl group of $Ni(dmit)_2$ anion is small, although not negligible. The perturbation caused by the hydrogen bond therefore may not give a serious effect on the oxidation state of the molecules.

The salt behaves as a semiconductor ($\sigma_{RT}=0.1$S cm^{-1}, $E_A=0.10$ eV) and no unusual behavior was observed within the entire range of the measurements. The result shows that the perturbation caused by the formation of the hydrogen bonding between the conduction column and the counter cation system was only a static one, and no dynamic effect appeared in the transport properties.

(HMemorph)$[Ni(dmit)_2]_2$ (3): Atomic parameters, selected bond lengths and angles are give in Table 4. Two crystallographically independent $Ni(dmit)_2$ molecules (A and B) construct a column along the $a+c$ direction. There are many intercolumnar side-by-side S···S contacts (minimum: 3.543(2) Å [S(8a)–S(1b)]). The aminium hydrogen of the *N*-methylmorpholinium ion forms a hydrogen bond with the thiocarbonyl group of the molecule B (Fig. 4). This is due presumably to the difference of "hydrogen bond acceptability" between thiocarbonyl and ether groups.[3a] Since the hydrogen bonding pattern is a simple pair-forming type, no higher order network is recognized in the crystal. The hydrogen bond strength is moderate, considering the N···S distance (3.389(5) Å [N(2c)···S(5b)]). Only a slight deviation from planarity is observed for both molecules A and B (max. deviation from each least-squares plane: 0.129(2) [S(10a)], 0.110(2) Å [S(5b)]), and their geometries are the same within the experimental errors. In contrast, the hydrogen-bonded $Ni(dmit)_2$ molecules (B) are pulled out from a regular stack of the column. As a result, A–$\overline{A}$ overlapping (distance=3.538(2) Å) is classified as Type I, while the other overlapping, B–$\overline{B}$ (3.580 (1) Å) and A–B (3.521(1) Å) belong to the Type II. Number of Type II overlapping is therefore three times larger than that of Type I, and the uniformity of the Ni-$(dmit)_2$ column is highly perturbed by these hydrogen bonds. This salt also showed a semiconductive behavior

(σ_{RT}=4 S cm^{-1}, E_A=0.10 eV). Relatively high σ_{RT} of **3** comparing to **2** mainly comes from the close packing of the molecule in the crystal, while the nonuniformity of the Ni(dmit)$_2$ column may lead to the activation-type transport behavior.

Summary In the crystal of **1**,**2**, and **3**, their structures are characterized by the existence of intermolecular hydrogen bonding between the counter ion system and Ni(dmit)$_2$ columns. Their stoichiometries, stacking modes and periodicities of the column are summarized in Table 5. In these salts, alignments of Ni(dmit)$_2$ molecules are mainly governed by the hydrogen bonding pattern. In the case of (Hmorph)$_2$[Ni(dmit)$_2$]$_3$ (**2**), neighboring Ni(dmit)$_2$ columns are linked by intermolecular hydrogen bonds, and as in the case of (ImH)[Ni(dmit)$_2$]$_2$ (ImH=imidazolium),[20] the higher order network of hydrogen bonds is constructed.

The trimeric structures are realized in **1** and **2**, because the periodicities of the cation system for **1** and **2** (=10 Å) are about three times of the separation of Ni(dmit)$_2$ slabs (3.5 Å). If the cation system has a periodicity of hydrogen bonding sites which is nearly commensurate to that of Ni(dmit)$_2$ molecules, acceptors will be forced to stack uniformly just as in the case of [Ni(*R*,*R*-chxn)$_2$Br]Br$_2$ (chxn=cyclohexane-1,2-diamine),[21] and good transport properties will therefore be realized. Utilization of a counter anion system connected with hydrogen bonds will give some insight in designing novel molecular conductors.

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