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Article

New 1:3 Type Nickel−Bis(dithiolene) Salt (FcCHCHPymCH₃)[Ni(dmit)₂]₃ (dmit: 2-Thioxo-1,3-dithiole-4,5-dithiolate): Its Electrocrystallization, Crystal Structure, Electrical Properties, and Electronic Band Structure Analysis

Yoon-Kyoung Han,[†] Dong-Kyun Seo,*,[‡] Haeyong Kang,[§] Woun Kang,[§] and Dong-Youn Noh*,[†]

Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea, Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, and Department of Physics, Ewha Womans University, Seoul 120-750, Korea

Black single crystals of Ni(dmit)₂ complex (dmit: 2-thioxo-1,3-dithiole-4,5-dithiolate) with *trans*-4-[2-(1-ferrocenyl)-vinyl]-1-methylpyridinium chromophore as a countercation, (FcCHCHPymCH₃)[Ni(dmit)₂]₃, were prepared by the electrocrystallization technique. In the triclinic structure of the complex ($P\bar{1}$, $a = 11.430(5)$ Å, $b = 13.349(2)$ Å, $c = 19.355(6)$ Å, $\alpha = 75.15(2)°$, $\beta = 79.19(3)°$, $\gamma = 82.12(2)°$, $Z = 2$), Ni(dmit)₂ anion layers are separated by the cations with a relatively rare 1:3 cation-to-anion ratio. Detailed crystal and electronic structure analysis revealed that the anions are stacked in the layers to form alternating dimers and monomers rather than trimers. The measured electrical conductivity indicates a semiconducting property of the compound with an estimated energy gap of 0.06 eV. The calculated LUMO bands are very narrow, and the semiconducting behavior is more likely due to the electron localization mainly on the dimers, consistent with the observed longer Ni–S bond distances in the dimers.

Introduction

The nickel complex (**1**) of dmit²⁻ (2-thioxo-1,3-dithiole-4,5-dithiolate) has been utilized to obtain molecular conductors, superconductors, magnets, and nonlinear optical materials, since the discovery of the first superconducting charge-transfer salt containing the transition-metal complex, TTF[Ni(dmit)₂].[1] The partially oxidized electronic state of the [Ni(dmit)₂]^{δ−} molecule ($δ < 1$) is an essential requirement for the high conductivity of the salts,[2] and yet previous research efforts have found that the stacking arrangements of the Ni(dmit)₂ molecules in the crystal structure are also very important in determining the magnitude of the orbital interactions between the adjacent complex molecules. Weak orbital interactions often provide Ni(dmit)₂ units bearing unpaired electrons, and their magnetic interactions are again governed by how the partially filled molecular orbitals (MOs) of Ni(dmit)₂ anions interact with each other. Therefore, to design customized functional materials from Ni(dmit)₂ salts having the requisite electronic properties, it is essential to understand the correlation between the electronic structures of the salts and the molecular arrangements in their crystal structure.

Among the many Ni(dmit)₂ salts studied so far, those compounds with an anion:cation ratio of 3 are rather rare, and only a handful of them have been reported in the literature.[1a,3−8] However, the reported stack modes of the Ni(dmit)₂ anion complex are extremely diverse, depending

* Author to whom correspondence should be addressed. E-mail: dynoh@swu.ac.kr.

† Seoul Women's University.

‡ Arizona State University.

§ Ewha Womans University.

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Chart 1
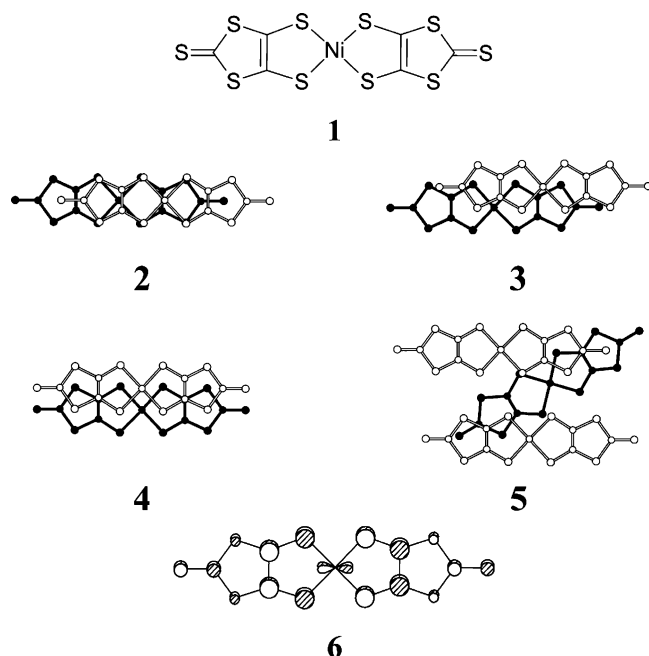
on the shapes and sizes of the countercations, as are the physical properties of the salts, which include metals, semimetals, semiconductors, and magnets. For a better understanding of our current work, we briefly review the previous findings, but we limit our scope only within the known 1:3 salts, since the relationships between stack modes and physical properties of the salts have been recognized and can be found in the literature.[1,3a]

In the crystal structure of semiconducting TPP[Ni(dmit)₂]₃ (TPP: tetraphenylphosphonium),[4] two of the three Ni(dmit)₂ species form two-dimensional sheets composed of stacks, and the remaining Ni(dmit)₂ unit exists almost perpendicular to the stacks, separating adjacent layers. In each stack within the layers, two overlap modes of the Ni(dmit)₂ units alternate, longitudinal offset (**2**) and transverse-longitudinal offset (**3**) (see Chart 1). The structure of metallic [AcrH][Ni(dmit)₂]₃ (AcrH: acridinium) contains anion layers made up of Ni(dmit)₂ stacks that are separated by AcrH countercation molecules.[6] Each layer of Ni(dmit)₂ molecules consists of alternating trimers and monomers: the trimers of Ni(dmit)₂ units overlap in a transverse offset mode (**4**), and monomers are sandwiched by the trimers in a so-called "spanning overlapping mode" (**5**). This spanning overlapping mode results in strong orbital interactions between the anions and,

hence, is known to be responsible for the two-dimensional metallic properties of a few Ni(dmit)₂ complexes, such as α-[Et₂Me₂N][Ni(dmit)₂]₂ and [*N,N*-dimethylpiperidinium]-[Ni(dmit)₂]₂.[9−11]

The formation of such trimers (or "triads") is rather common among the 1:3 compounds, although the detailed stacking modes can vary considerably. The replacement of AcrH by PheH (phenazinium), a structurally similar cation, affords another 1:3 compound but with a semiconducting property.[6] In the crystal structure of [PheH][Ni(dmit)₂]₃, the Ni(dmit)₂ trimers are formed in the transverse offset mode (**4**), and then the trimers stack themselves in the transverse-longitudinal offset mode (**3**). Another example of the same stacking pattern is the [Co(η-C₅H₅)₂][Ni(dmit)₂]₃ structure.[5] A more recently reported complex, [bmim][Ni(dmit)₂]₃ (bmim = 1-butyl-3-methylimidazolium), exhibits trimers in its structure that are formed by almost completely (face-to-face; not shown here) overlapping Ni(dmit)₂ units, and yet these trimers are stacked in the longitudinal offset mode (**2**).[7] The semiconducting properties of all of these compounds likely result from the weak orbital interactions between the Ni(dmit)₂ units, as indicated by the unpaired electrons observed from the magnetic studies of these compounds.

In the course of our recent efforts to incorporate large asymmetric countercations into conducting salts for large changes in their stacking patterns and physical properties,[12] we prepared another semiconducting 1:3 Ni(dmit)₂ salt with the FcCHCHPymCH₃ cation. In this report, we describe the synthesis, crystal structure, and electrical properties of the [FcCHCHPymCH₃][Ni(dmit)₂]₃ salt and discuss its electronic structure in comparison with those of other 1:3 type salts that appeared in the previous studies.

Experimental Section

Synthesis. All chemicals were of reagent grade and were used without further purification. Solvents were purified prior to use according to the literature method.[13] The preparation of the title compound was carried out first by preparing the starting material, (*n*-Bu₄N)[Ni(dmit)₂].[14] After the following substitution of the *n*-Bu₄N cation by FcCHCHPymCH₃ cation, the title compound was electrochemically crystallized from (FcCHCHPymCH₃)[Ni(dmit)₂] as detailed below. The synthesis for (FcCHCHPymCH₃)CF₃SO₃ was carried out according to the reported procedures.[15] The analytical data for the compounds coincided well with the literature values.

***trans*-4-[2-(1-Ferrocenyl)vinyl]-1-methylpyridinium Bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate, (FcCHCHPymCH₃)-[Ni(dmit)₂].** To an acetonitrile solution (40 mL) of (*n*-Bu₄N)[Ni-

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Table 1. Crystal and Structure Refinement Data for (FcCHCHPymCH₃)[Ni(dmit)₂]₃

empirical formula	$C_{36}H_{18}FeNNi_3S_{30}$
fw	1658.29
cryst system	triclinic
space group	$P\bar{1}$
$a/\text{Å}$	11.430(5)
$b/\text{Å}$	13.349(2)
$c/\text{Å}$	19.355(6)
α/deg	75.15(2)
β/deg	79.19(3)
γ/deg	82.12(2)
$V\,(\text{Å}^3)$	2791.5(16)
Z	2
GOF on F^2	1.155
R1 (wR2) $[I > 2\sigma(I)]^a$	0.0655 (0.1360)
R1 (wR2) (all data)^a	0.0796 (0.1449)

^{a} $R_1 = \sum\lVert F_o\rvert - \lvert F_c\rVert / \sum\lvert F_o\rvert$. $wR_2 = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4\}^{1/2}$, where $w = 1/\{\sigma^2 F_o{}^2 + (aP)^2 + bP\}$.

(dmit)₂] (69.2 mg, 0.1 mmol) was added an excess amount of (FcCHCHPymCH₃)CF₃SO₃ (136 mg, 0.3 mmol) dissolved in acetonitrile (12 mL). The mixture was stirred for 40 min at room temperature. The polycrystalline product was obtained by filtration and washed with ethanol. Yield: 79%. FT-IR (KBr, cm⁻¹): 1596 (Py C−C), 1345 (C=C), 1192, 1198 (Py C−H), 822, 484 (Fe−Cp).

Single Crystals of *trans*-4-[2-(1-Ferrocenyl)vinyl]-1-methyl-pyridinium Tris[bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickel-ate], (FcCHCHPymCH₃)[Ni(dmit)₂]₃. Single crystals of the 1:3 complex were grown by the typical electrochemical crystallization method under an Ar atmosphere. (FcCHCHPymCH₃)[Ni(dmit)₂] (7.56 mg, 0.01 mmol) and (FcCHCHPymCH₃)CF₃SO₃ (13.5 mg, 0.03 mmol) electrolytes were put in each compartment of an H-type cell and dissolved in freshly distilled acetonitrile. A constant current of 1.2 μA was applied for 7 days in a dark place. The black needlelike crystals grown on the Pt electrode (i.d. = 1.0 mm) were filtered out, washed with acetonitrile and methanol, and dried in air. Yield: 19%. FT-IR (KBr, cm⁻¹): 1320, 1239 (C=C), 1052 (C=S), 493 (S−C−S).

Single-Crystal X-ray Structure Determination. A black block-shaped crystal was mounted on a thin glass rod with epoxy glue. The crystal was transferred to an Enraf-Nonius CAD4 automated diffractometer equipped with a graphite-monochromated Mo Kα radiation source ($\lambda = 0.710\,73$ Å) at 293(2) K. The orientation matrix and unit cell parameters were determined for the data collection from 25 machine-centered reflections in the 2θ range from 15 to 25°. A total of 4304 reflections were found in a hemisphere with $\theta_{min} = 1.59°$ and $\theta_{max} = 25.47°$ ($0 \le h \le 13$, $-15 \le k \le 16$, $-22 \le l \le 23$), and 4123 were independent among which 3592 had intensities greater than $2\sigma(I)$. The structure was solved and refined using SHELXS-86[16] and SHELXL-97,[17] respectively, and atomic scattering factors for all non-hydrogen atoms were supplied by the SHELX-86 system. The full-matrix least-squares refinement converged at $R_1 = 8.0\%$, $wR_2 = 14.5\%$, and GOF = 1.16 for 643 variables and 4123 reflections. The crystallographic parameters and procedural information corresponding to the data collection are given in Table 1, and selected bond lengths and angles are listed in Table 2.

Measurements of IR Spectra and Electrical Conductivities. The infrared spectra were recorded at room temperature by employing the KBr method on a MIDAC FT-IR spectrometer. A

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for (FcCHCHPymCH₃)[Ni(dmit)₂]₃^a

Ni(1)−S(1)	2.138(4)	Ni(1)−S(2)	2.144(4)
Ni(2)−S(6)	2.148(4)	Ni(2)−S(7)	2.133(4)
Ni(3)−S(11)	2.162(5)	Ni(3)−S(12)	2.163(5)
Ni(3)−S(16)	2.144(5)	Ni(3)−S(17)	2.148(5)
Ni(4)−S(21)	2.154(5)	Ni(4)−S(22)	2.152(5)
Ni(4)−S(26)	2.148(5)	Ni(4)−S(27)	2.168(5)
S(1)−C(1)	1.669(15)	S(2)−C(2)	1.678(18)
S(6)−C(4)	1.711(17)	S(7)−C(5)	1.678(15)
S(11)−C(7)	1.730(16)	S(12)−C(8)	1.706(18)
S(16)−C(10)	1.703(16)	S(17)−C(11)	1.715(15)
S(21)−C(13)	1.684(15)	S(22)−C(14)	1.689(15)
S(26)−C(16)	1.718(16)	S(27)−C(17)	1.702(16)
C(1)−C(2)	1.385(19)	C(4)−C(5)	1.415(19)
C(7)−C(8)	1.342(21)	C(10)−C(11)	1.401(19)
C(13)−C(14)	1.396(19)	C(16)−C(17)	1.354(20)
C(28)−C(29)	1.45(3)	C(29)−C(30)	1.35(3)
C(30)−C(31)	1.43(3)		
S(1)−Ni(1)−S(2)	92.61(17)	S(1)−Ni(1)−S(2)$^{\#1}$	87.39(17)
S(7)−Ni(2)−S(6)	92.76(17)	S(7)−Ni(2)−S(6)$^{\#2}$	87.24(17)
S(16)−Ni(3)−S(17)	92.66(18)	S(16)−Ni(3)−S(11)	88.29(19)
S(17)−Ni(3)−S(11)	178.6(2)	S(16)−Ni(3)−S(12)	178.6(2)
S(17)−Ni(3)−S(12)	86.13(18)	S(11)−Ni(3)−S(12)	92.93(19)
S(26)−Ni(4)−S(22)	178.2(2)	S(26)−Ni(4)−S(21)	87.06(18)
S(22)−Ni(4)−S(21)	92.70(18)	S(26)−Ni(4)−S(27)	93.01(18)
S(22)−Ni(4)−S(27)	87.28(18)	S(21)−Ni(4)−S(27)	178.5(2)

^{a} Symmetry operations: (#1) $1 - x$, $-y$, $1 - z$; (#2) $2 - x$, $1 - y$, $1 - z$.

standard four-probe technique was used to measure the temperature-dependent conductivity for two well-shaped single crystals of the title complex. Silver paste was used for the electrical contact with four thin gold wires, and the conductivities were measured with lock-in amplifiers tuned at a low frequency.

Results and Discussion

Crystal Structure Analysis. Figure 1 shows four crystallographically independent Ni(dmit)₂ units and two FcCH-CHPymCH₃ cations in the structure of the title compound, with the atomic numbering scheme. The four Ni(dmit)₂ units are denoted as [Ni1], [Ni2], [Ni3], and [Ni4], hereafter, according to the numbering scheme for the central Ni atoms. The two FcCHCHPymCH₃ cations are equivalent by an inversion symmetry. The crystal structure exhibits the Ni(dmit)₂ layers that are separated by cation layers in an alternating way (Figure 2) along the *c*-axis. Each layer of Ni(dmit)₂ molecules consists of two stacks, A and B, which run parallel along the *b*-axis. One [Ni1] and two [Ni3] molecules form a repeating unit of the stack A, and the stack B consists of one [Ni2] and two [Ni4] molecules. These two stacks are alternately packed in a side-by-side mode in the *ab*-plane. A side view of stack B (or stack A) is shown in Figure 3. Each stack can be expressed as a repeating pattern of the monomer and the dimer, such as ---([Ni1]−[Ni3][Ni3])--- in stack A and ---([Ni2]−[Ni4][Ni4])--- in stack B, rather than a repeating pattern of the trimers. The average intradimer distances are 3.573 Å for stack A ([Ni3]⋯[Ni3]) and 3.517 Å for stack B ([Ni4]⋯[Ni4]), with the overlap in each stack in a transverse offset mode (**4**), and the average distances between the monomer and the dimer are 3.594 Å for stack A ([Ni1]⋯[Ni3]) and 3.581 Å for stack B ([Ni2]⋯[Ni4]), which are longer than the corresponding intradimer distances, with the two stacks over-

(a)

(b)
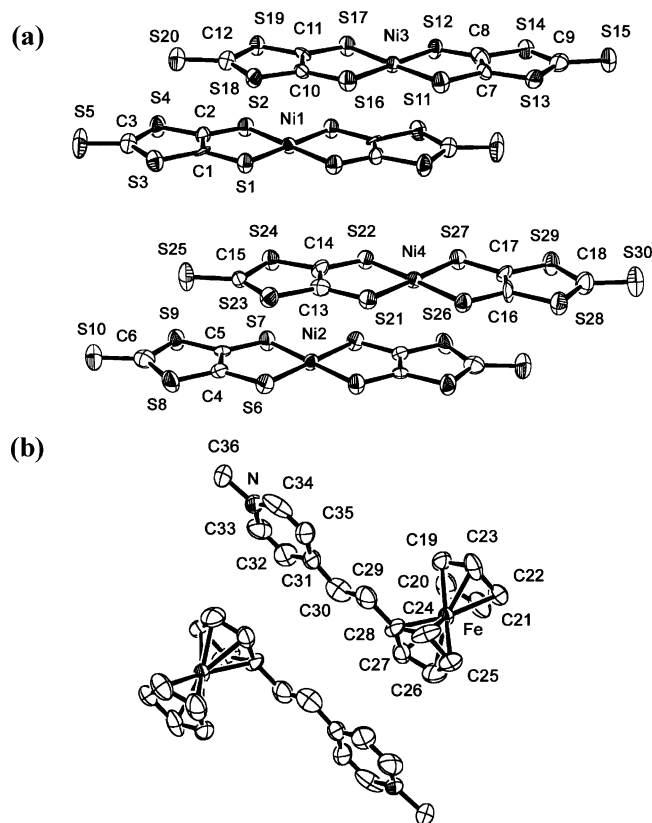
Figure 1. Perspective view of (a) four independent $Ni(dmit)_2$ units and (b) $FcCHCHPymCH_3$ cations with atomic numbering scheme.
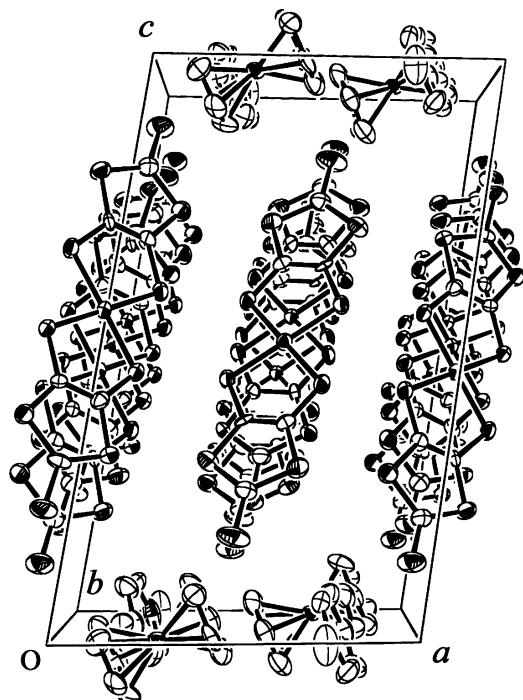

Figure 2. Crystal structure of $(FcCHCHPymCH_3)[Ni(dmit)_2]_3$. Stack A is located inside the unit cell, and stack B is on the face (*bc*-plane) of the unit cell.

lapping in transverse-longitudinal offset mode (**3**). These distances are very similar to those found in $[PheH][Ni(dmit)_2]_3$ (3.49 and 3.58 Å) but slightly larger than those in $[AcrH]$-$[Ni(dmit)_2]_3$ (3.49 and 3.10 Å).[6] In this plane, the packing
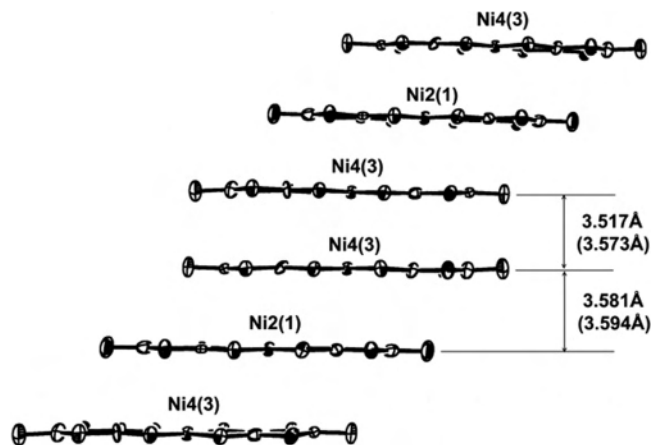
Figure 3. Repeating pattern of $Ni(dmit)_2$ units in stack B. Stack A shows the same repeating pattern. The numbers in parentheses denote the intermolecular distances for stack A.
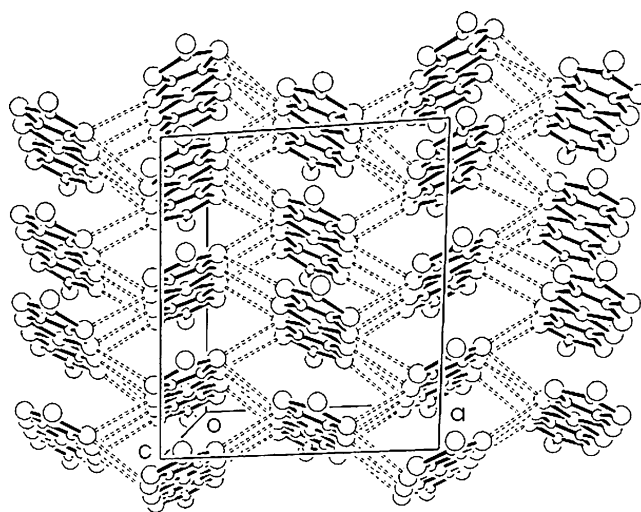

Figure 4. Projection view of a single layer of $Ni(dmit)_2$ units in the *ab*-plane. The intermolecular S···S close contacts shorter than 3.7 Å are indicated by dotted lines.

of the $Ni(dmit)_2$ stacks is very favorable for obtaining a large number of intermolecular S···S contacts, which are known to be responsible for high conductivity. Intermolecular S···S contacts shorter than 3.70 Å, the sum of the van der Waals radii,[18] are to be found between the $Ni(dmit)_2$ stacks (see Supporting Information), as represented by the dotted line in Figure 4, clearly demonstrating that the $Ni(dmit)_2$ layer in the *ab*-plane consists of a two-dimensional network connected by short S···S contacts. The countercations adopt a dimeric arrangement in face-to-face and head-to-tail modes (Figure 1b), and they form layers between the $Ni(dmit)_2$ layers.

The NiS_4 core is slightly distorted from regular square planar geometry, judging from the Ni−S distances and S−Ni−S angles listed in Table 2. The Ni−S distances of the $Ni(dmit)_2$ anions range from 2.133 to 2.168 Å, for which the average distances are 2.141 Å for the [Ni1] and [Ni2], and 2.155 Å for the [Ni3] and [Ni4]. These distances seem to be comparable to the average Ni−S distance in the

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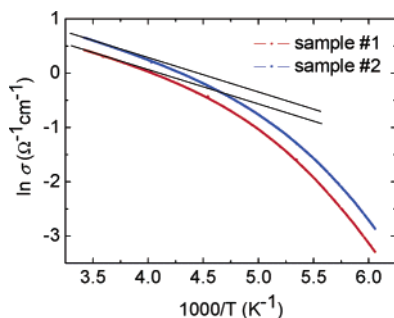
Figure 5. Temperature-dependent electrical conductivities of two different samples of (FcCHCHPymCH₃)[Ni(dmit)₂]₃.

Figure 6. LUMO bands calculated for a layer of Ni(dmit)₂ molecules in *ab*-plane for (a) [FcCHCHPymCH$_3$][Ni(dmit)$_2$]$_3$ ($Z = 2$) and (b) [PheH]-[Ni(dmit)$_2$]$_3$ ($Z = 1$) by the extended Hückel tight binding method. $\Gamma = (0, 0)$, $X = (a*/2, 0)$, $Y = (0, b*/2)$, and $M = (a*/2, b*/2)$.

corresponding 1:1 complex (2.164 Å).[12b] The C=C bond distances of the Ni(dmit)$_2$ units range from 1.342 to 1.415 Å, with the average distance (1.381 Å) being very close to those of (TPP)[Ni(dmit)$_2$]$_3$ (1.38(1) Å)[4a] and [Co(η-C$_5$H$_5$)$_2$]-[Ni(dmit)$_2$]$_3$ (1.39(2) Å).[5] In a comparison of the title compound with the corresponding 1:1 complex (1.373 Å),[12b] the relationship between the C=C bond distance and the oxidation number of the Ni(dmit)$_2$ unit[19] is not obviously observed.

The countercation in the title complex is a well-known 2nd NLO chromophore that consists of an electron-donating ferrocene group and an electron-accepting methylpyridinium group connected by an ethylene moiety. The degree of communication between these two groups was able to be evaluated using the ratios of the bond distances, d(C28−C29)/d(C29−C30) and d(C30−C31)/d(C29−C30). These ratios were calculated as being 1.07 and 1.06, respectively, for the title complex. These values are obviously smaller than those of the corresponding 1:1 complex (1.11 and 1.10, respectively)[12b] and even smaller than those of (FcCHCHPymCH$_3$)-NO$_3$ (1.21 and 1.28, respectively).[15] This means that the electronic communication between the electron-donor and acceptor groups is expected to be more facile in the 1:3 complex than in the 1:1 complex or in (FcCHCHPymCH$_3$)-NO$_3$. Therefore, the 1:3 complex could well be a more efficient 2nd NLO material if we could overcome the structural problem of centrosymmetry.[20]

Electrical Conductivity. Presented in Figure 5 is an Arrhenius plot of the electrical conductivity of (FcCH-CHPymCH$_3$)[Ni(dmit)$_2$]$_3$ measured using two samples chosen from the same batch. The conductivities of the two samples (#1 and #2) at room temperature were 1.52 and 1.90 Ω^{-1} cm^{-1}, respectively. These values are very close to those of TPP[Ni(dmit)$_2$]$_3$[4] and [PheH][Ni(dmit)$_2$]$_3$[6] but higher than that of [AcrH][Ni(dmit)$_2$]$_3$.[6] The small difference in conductivity between our two samples is mainly due to the uncertainty of measuring the sample cross section. The temperature dependence of the conductivity could not be explained in terms of a single direct gap semiconductor. The
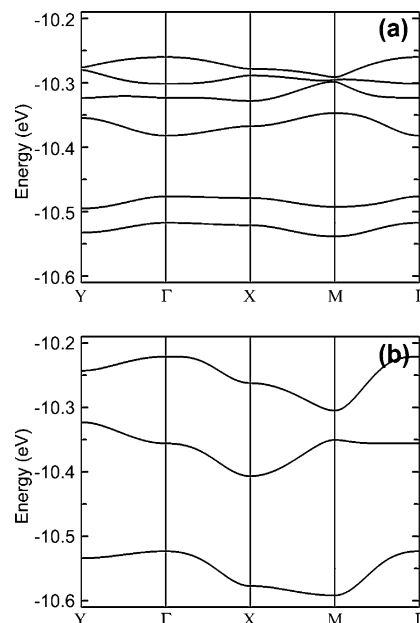
initial slope of the Arrhenius plot gives an estimated value for the energy gap of 0.06 eV.

Electronic Band Structure Analysis. We examined the electronic structure of a single Ni(dmit)$_2$ layer (Figure **4**) in the *ab*-plane of (FcCHCHPymCH$_3$)[Ni(dmit)$_2$]$_3$ using the extended Hückel tight-binding method.[21,22] The layer has six Ni(dmit)$_2$ molecules per unit cell, and Figure 6a shows six bands (LUMO bands hereafter) that are primarily from the LUMO's of the Ni(dmit)$_2$ molecules. With the oxidation state [Ni(dmit)$_2$]$_3^-$, there are two electrons to fill the LUMO bands per unit cell, and hence without a strong electron repulsion the two electrons will fill the lowest LUMO band in our calculated band structure (Figure 6a). Because there is no overlap between HOMO and LUMO bands, the following discussions are based solely on the LUMO bands that are near the Fermi level. While the LUMO bands span in a relatively wide energy region from −10.53 to −10.24 eV, all the six bands are narrow. In particular, the two lowest bands are well separated from the upper bands and have their bandwidths smaller than 0.05 eV. As discussed below, the observed narrow bands indicate a possible Mott−Hubbard behavior of the salt, which is consistent with its electrical property.

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(22) All of the calculation results in this work were obtained using a single-ζ basis set for the nonmetallic atoms and a double-ζ basis set for Ni. A weighted H_{ij} formula was used for the extended Hückel calculations, and for all of the calculations, the following atomic parameters were employed (H_{ii} = orbital energy, ζ = Slater component, c = coefficient): Ni 4s −9.17 eV, 1.825, 4p −5.15, 1.125, 3d −13.49, ζ_1 = 5.75, c_1 = 0.568, ζ_2 = 2.00, c_1 = 0.629; C 2s −21.4 eV, 1.625, 2p −11.4 eV, 1.625; S 3s −20.0 eV, 1.817, 3p −13.3 eV, 1.817.

Table 3. Comparison of Stacking Patterns and Selected Structural and Electronic Features of the Individual Ni(dmit)₂ Molecules in [FcCHCHPymCH₃][Ni(dmit)₂]₃ and [PheH][Ni(dmit)₂]₃

	[FcCHCHPymCH₃][Ni(dmit)₂]₃		[PheH][Ni(dmit)₂]₃[d]
	stack A	stack B	
stacking pattern[a]	---(monomer−dimer)---	---(monomer−dimer)---	---(trimer)---
	---([Ni1]−[Ni3][Ni3])---	---([Ni2]−[Ni4][Ni4])---	---([Ni1][Ni2][Ni1])---
$\bar{d}$([Ni]···[Ni])[b] (Å)	3.573 in [Ni3]···[Ni3]	3.517 in [Ni4]···[Ni4]	3.49 in [Ni2]···[Ni1]
	3.594 in [Ni1]···[Ni3]	3.581 in [Ni2]···[Ni4]	3.58 in [Ni1]···[Ni1]
$\bar{d}$(Ni−S) (Å)	2.142 in [Ni1]	2.141 in [Ni2]	2.163 in [Ni2]
	2.154 in [Ni3]	2.156 in [Ni4]	2.150 in [Ni1]
E(LUMO)[c] (eV)	−10.35 in [Ni1]	−10.33 in [Ni2]	−10.51 in [Ni2]
	−10.49 in [Ni3]	−10.45 in [Ni4]	−10.41 in [Ni1]

[a] Designation of monomer, dimer, and trimer is based on the stacking modes. Within an *n*-meric unit, the molecules are stacked in a transverse offset mode (**4**). They are in the transverse-longitudinal offset mode (**3**) between the neighboring *n*-meric units. [b] The average intermolecular distances between two neighboring Ni(dmit)₂ molecules that are parallel to each other in the same stack. [c] The LUMO energies were calculated for individual Ni(dmit)₂ molecules by neglecting intermolecular orbital interactions. [d] Reference 6.
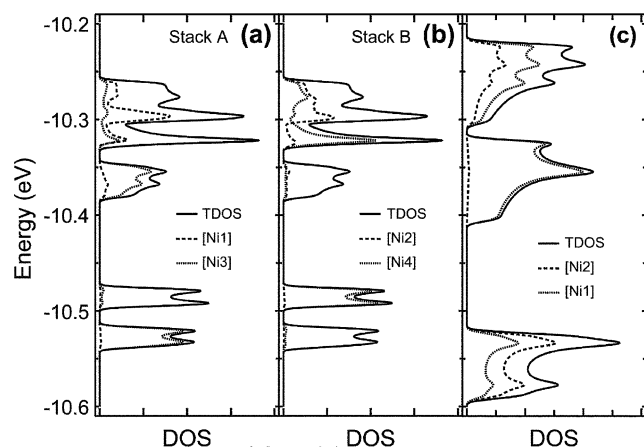

Figure 7. Projected densities of states (PDOSs) of the LUMO bands in Figure 6. (a) and (b) present the PDOSs of the Ni(dmit)₂ molecules in stacks A and B, respectively, in [FcCHCHPymCH₃][Ni(dmit)₂]₃. The PDOSs of the Ni(dmit)₂ molecules in [PheH][Ni(dmit)₂]₃ are shown in (c). The solid lines indicate the total DOSs. The dashed and dotted lines represent two different types of Ni(dmit)₂ molecules that exist with one and two units per unit cell, respectively.

The corresponding projected densities of states (PDOSs) of the four different Ni(dmit)₂ molecules, [Ni1]−[Ni4], are presented in Figure 7a,b for stacks A and B, respectively, as the summations of the contributions of all the atoms in individual molecules. In Figure 7a,b, the contributions of the monomers, [Ni1] and [Ni2], are localized in the two bands at the top in the energy region between −10.31 and −10.24 eV. The band energies are close to the LUMO energies of [Ni1] and [Ni2] (−10.35 and −10.33 eV, respectively; Table 3) that were calculated without taking into account the intermolecular interactions, and this agrees with the monomeric nature of the [Ni1] and [Ni2] in the structure. Meanwhile, the first and the third bands from the bottom are mainly from [Ni3] dimers in stack A and the second and the forth bands are from [Ni4] dimers in stack B. Although not shown here, a detailed orbital analysis revealed that the lower and upper bands from each stack correspond to the bonding and antibonding combinations of the dimers. The calculated LUMO energies of the isolated [Ni3] and [Ni4] molecules were ca. −10.5 eV (Table 3), and the bonding and antibonding bands in Figure 7a,b are stabilized approximately by −0.04 eV and destabilized by 0.1 eV, respectively, by the formation of the [Ni3] and [Ni4] dimers.

In essence, the calculated band structure of the compound can be well understood based on the ---(monomer−dimer)--- stacking pattern found structurally. Besides the modulation within the stacks, the weak interstack orbital interactions, as noted from the good separation of PDOSs of the molecules in different stacks, are responsible for the very narrow LUMO bands.

It is worth examining how the stacking patterns (**3** and **4**) found in (FcCHCHPymCH₃)[Ni(dmit)₂]₃ affect the strength of the orbital interactions of the Ni(dmit)₂ within the stacks. In fact, it has been recognized in the literature that the longitudinal offset (**2**) in the stacks effectively reduces the orbital interactions between the LUMO orbitals of neighboring Ni(dmit)₂ molecules.[23] For an ideal Ni(dmit)₂ molecule with D_{2h} symmetry (**1**), the orbital coefficients of the LUMO (**6**) change their signs rapidly along the longitudinal direction. When the Ni(dmit)₂ units are stacked in a longitudinal offset mode (**2**), therefore, the intermolecular interactions in the LUMO energy bands are effectively diminished because of the opposite sign of their orbital coefficients. The same result is expected for a transverse longitudinal offset mode (**3**), and this is the stacking mode between a Ni(dmit)₂ monomer and its neighboring molecules in the dimers in the (FcCHCHPymCH₃)[Ni(dmit)₂]₃ structure. Such severe changes in orbital interactions are not expected when the molecules are offset transversely (**4**) as the Ni(dmit)₂ molecules do within the dimers of the (FcCHCHPymCH₃)[Ni(dmit)₂]₃. It is because of the symmetric nature of the LUMO with respect to the reflection plane perpendicular to the transverse direction.

In Table 3, another notable feature is that average Ni−S bonds of the Ni(dmit)₂ molecules in the dimers are slightly longer than those in the monomers by ∼0.01 Å. While further studies are necessary, this behavior is not inconsistent with the antibonding character between the Ni d-orbital and the π-orbitals of the neighboring S atoms which the additional electrons fill in. The effect of these additional electrons is expected to be smaller on bond distances in the dmit molecules due to weaker π-bonding than σ-bonding of the dmit. Whether the electrons are localized only in the [Ni3] dimers is not clear, although that will be more likely just based on the calculated electronic structure (Figure 7a,b).

(23) Canadell, E. *Coord. Chem. Rev.* **1999**, *185−186*, 629.

However, the longer Ni−S bonds *both* in the [Ni3] and [Ni4] molecules, as well as their consequently stabilized LUMOs, implies that the latter's LUMO is also occupied. Given two extra electrons per unit cell of the layers, this should result in one unpaired electron in each Ni(dmit)₂ dimer. While this prediction has to be checked experimentally, this electronic picture is reasonable, considering the very narrow LUMO bands in Figure 6.[24] Unfortunately, we were not yet able to prepare an enough amount of the sample for magnetic property studies.

An explicit treatment of large electron repulsion energies has been carried out previously in the electronic structure calculations of [PheH][Ni(dmit)₂]₃. It is another semiconducting 1:3 compound that has similar layers formed by two structurally inequivalent types of Ni(dmit)₂ molecules, [Ni1] and [Ni2], with a 2:1 ratio.[6] The molecules of this compound form [Ni1][Ni2][Ni1] trimers which repeat to form stacks, in such a way that they overlap in a transverse offset mode (**4**) within the trimers but in a transverse-longitudinal offset mode (**3**) between neighboring trimers. For the purpose of comparison, we recalculated the band structure of this compound using the extended Hückel tight binding method. In the calculated band structure (Figure 6b), the existence of three narrow and well-separated LUMO bands, from three Ni(dmit)₂ molecules per unit cell, is in good agreement with the previous calculation results.[6] The three LUMO bands are narrow with bandwidths smaller than 0.1 eV and are well separated,[25] as in the case of the [FcCHCHPymCH₃][Ni-(dmit)₂]₃. The semiconducting property of the compound has been explained in terms of electron repulsions that are significant in the narrow bands.[6] This Mott−Hubbard behavior is likely true for the [FcCHCHPymCH₃][Ni(dmit)₂]₃ in our work, as we observe even narrower LUMO bands in the calculated electronic structure.

However, a drastic difference in the electronic structures between the two compounds is noticed when we examine the contributions of the LUMO orbitals of the [Ni1] and [Ni2] molecules in the [PheH][Ni(dmit)₂]₃. Figure 7c shows the PDOSs of the LUMOs from two different types of [Ni(dmit)₂] molecules, [Ni1] and [Ni2], in the [PheH]-[Ni(dmit)₂]₃. It is noted that the middle band is mainly from [Ni1], i.e., the terminal Ni(dmit)₂ molecules of the [Ni1][Ni2][Ni1] trimers, while the top and bottom bands are dominated by the central [Ni2] molecule. This is analogous to the σ-type electronic structure of linear triatomic hypervalent molecules, such as I₃⁻ and Te₃⁴⁻. In their structure, three σ-type p-orbitals, each on different atoms, form bonding, nonbonding, and antibonding MOs in the order of increasing energy.[26,27] The bonding and antibonding MOs have a larger contribution from the central atom, while the

nonbonding MO is derived solely from the two symmetrically equivalent terminal atoms. If the hypervalent molecules were arranged linearly in a repetitive pattern, the resultant chain would exhibit the same band structure that a Ni(dmit)₂ stack in the [PheH][Ni(dmit)₂]₃ has, with three LUMOs in a unit cell. The LUMO energy calculated for an isolated [Ni1] is −10.41 eV (Table 3), which is close to the energy of the band in the middle, and this agrees with the nonbonding nature of the band with the large [Ni1] contribution. The LUMO of an isolated [Ni2] has energy of −10.51 eV, which is 0.10 eV lower than that of [Ni1]. This is due to the fact that the observed average Ni−S bond distance is longer in [Ni2] than in [Ni1] (Table 3). It is noted that the partially filled band of the [PheH][Ni(dmit)₂]₃ is mainly from the [Ni2];[28] i.e., the unpaired electron is more likely to stay on the [Ni2], the central molecule in the trimers, than on either of the [Ni1] molecules, i.e., the terminal ones. There have not been any electronic structure studies on other 1:3 type Ni(dmit)₂ salts, and yet it is likely that their electronic structures resemble that of [PheH][Ni(dmit)₂]₃ due to the formation of trimers in common.

Conclusion

By using the FcCHCHPymCH₃ chromophore as a countercation in an electrochemical crystallization, we prepared single crystals of the [FcCHCHPymCH₃][Ni(dmit)₂]₃ compound. With the relatively uncommon 1:3 cation-to-anion ratio, the crystal structure of the compound exhibits monomer−dimer repeating units in two inequivalent stacks of the Ni(dmit)₂ molecules. The detailed theoretical examination of its electronic structure revealed that this new stacking pattern, among the 1:3 type salts, endows the [FcCH-CHPymCH₃][Ni(dmit)₂]₃ compound with a markedly different electronic nature, as compared to other closely related compounds, even though their semiconducting property remains as a common feature. The semiconducting property is likely due to the Mott−Hubbard nature of the electronic structure of the compound which is expected from the weak orbital interactions between the Ni(dmit)₂ molecules and from the structural features of the molecules in the compound.

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(25) There is only one type of Ni(dmit)₂ stack that is involved in forming the layers, and hence only three LUMO bands appear in the band structure.

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(28) Considering the 2:1 mole ratio between [Ni1] and [Ni2], the contribution of [Ni1] to the lowest LUMO band in Figure 7c is just a quarter of that of [Ni2].