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Substituent Effects on Formation of Cation Dimers by Weak Hydrogen Bonds in Crystals of Carbonyl Pyridinium Salts of Ni(dmit)$_2$

Kazuaki Tomono,* Ayako Koyano, Takashi Morita, and Kazuo Miyamura

Department of Chemistry, Faculty of Science, Tokyo University of Science,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

Received January 26, 2009; E-mail: 1303667@may.rikadai.jp

Five 1:1 salts of 3-X-1-methylpyridinium (X = benzoyl, acetyl, methoxycarbonyl, carboxy, and aminocarbonyl; abbreviated as Ben, Ace, Met, Car, and Ami, respectively) cations with a $[\mathrm{Ni(dmit)_2}]^-$ anion ($[\mathrm{Ben}]^+[\mathrm{Ni(dmit)_2}]^-$ (**1**), $[\mathrm{Ace}]^+[\mathrm{Ni(dmit)_2}]^-$ (**2**), $[\mathrm{Met}]^+[\mathrm{Ni(dmit)_2}]^-$ (**3**), $[\mathrm{Car}]^+[\mathrm{Ni(dmit)_2}]^-$ (**4**), and $[\mathrm{Ami}]^+[\mathrm{Ni(dmit)_2}]^-$ (**5**)) have been synthesized and characterized by single-crystal X-ray analysis and conductivity measurements. In the crystals, three cations **1**–**3** were found to form dimers by weak C–H···O hydrogen bonds, and the arrangements of cations had a strong relation with the electronic effect of the substituents. The cations of **1**–**3** formed similar centrosymmetrically associated dimers constructed by weak C–H···O hydrogen bonds, whose geometric parameters had a correlation with the electronic effect of the substituents. A cation of **4** also formed centrosymmetrically associated dimer, but it was made by an O–H···O hydrogen bond as usually observed in the case of carboxylic acid. In contrast with other complex salts, cations of **5** formed one-dimensional structure by C–H···O hydrogen bonding. The conductivities of salts **1**, **2**, **3**, **4**, and **5** at room temperature were 1.00×10^{-6}, 1.10×10^{-6}, 2.86×10^{-6}, 9.77×10^{-6}, and $8.75 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$, respectively.

Physical properties of molecular conductors depend on the molecular alignment in crystals. However, prediction of the molecular alignment within a crystal 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. That is why compounds often exhibit polymorphism. On the other hand, hydrogen bonding has a strictly fixed orientation, and this intermolecular interaction forms a characteristic structure in the crystal. The bonding schemes are therefore predictable to a certain extent.[1,2] Furthermore, non-covalent intermolecular forces play a major role in determining the crystal structure, i.e., especially for dielectric material and biological macromolecules.[3,4] As for the intermolecular interaction, the focus has been on the hydrophilic interaction; X–H···Y (X = O, N and Y = O, N, and halogen) hydrogen bonds are generally considered to be a major force in selective and/or specific molecular recognition. However, it has become accepted that supramolecular assemblies are achieved not only by strong hydrogen bonds such as above-mentioned O–H···O and N–H···O, but also by weak C–H···O hydrogen bonds. The importance of C–H···O hydrogen bonding is now widely recognized especially in forming desired crystal structures. The understanding and utilization of all non-covalent 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.[5–12] The present study aims at investigating the importance of weak hydrogen bonding (especially C–H···O hydrogen bonds) in the crystals of metal complex salts and its influence on aggregated structure of the cation domain to the cation domain of aggregate form and also on geometric parameters by means of single-crystal X-ray analysis and IR spectroscopy.

The metal complex Ni(dmit)$_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) has been widely studied as a conductor or a magnetic material.[13–15] Up to now, eleven molecular superconductors based on metal complexes of dmit ligand have been discovered.[16–24] The counter cations used in the M(dmit)$_2$ salts can be closed shell as well as open shell cations. The former cations do not make any contribution to the conduction path, although their shapes and sizes play a crucial role on the mode of stacking of anion complexes, which will determine the electrical properties of the salts. Since the discovery of the first closed shell molecular superconductor $[\mathrm{N(CH_3)_4}][\mathrm{Ni(dmit)_2}]_2$,[17] closed shell cations used so far have been mostly of the tetraalkylammonium type. To date, we have been exploring methods to control the Ni(dmit)$_2$ arrangement by regulating intermolecular interaction of chemically modified cations.[25–28] As shown in our previous report,[25] the use of geometric isomers of methoxycarbonyl-1-methylpyridinium as cation resulted in formation of cation aggregate by weak C–H···O hydrogen bonds in crystal structure. The synthesis of such Ni(dmit)$_2$ complex salt has drawn our attention to the role of weak C–H···O hydrogen bonding involving carbonyl groups, because such a weak interaction between cations (especially in metal complex crystals) has not been discussed in detail.

In this study, in order to examine the ability of remarkably weak C–H···O hydrogen bonds and the effect of electron-releasing substituents in cations of the Ni(dmit)$_2$ salts, we used five pyridinium derivatives. The five counter cations of the $[\mathrm{Ni(dmit)_2}]^-$ complex used are 3-benzoyl-1-methylpyridinium (abbreviated as Ben), 3-acetyl-1-methylpyridinium (abbreviated as Ace), 3-methoxycarbonyl-1-methylpyridinium (abbreviated as Met), 3-carboxy-1-methylpyridinium (abbreviated as Car), and 3-aminocarbonyl-1-methylpyridinium (abbreviated

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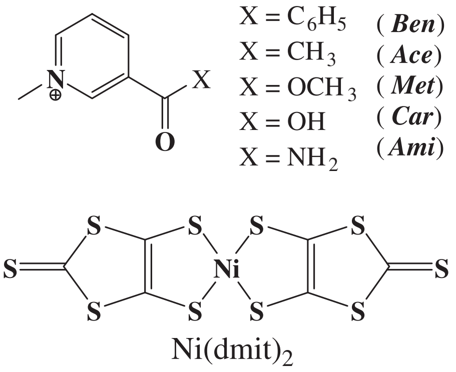


Chart 1.

as Ami) ions. The functional groups $-C_6H_5$, –Me, –OMe, –OH, and $-NH_2$ used in these cations are known as substituents leading to ortho and para isomers in the substitution reaction of benzene rings particular for electron-releasing substituents. The electron-releasing ability is also in this order.[29] Hereafter, the crystals of $[Ben]^+[Ni(dmit)_2]^-$, $[Ace]^+[Ni(dmit)_2]^-$, $[Met]^+[Ni(dmit)_2]^-$, $[Car]^+[Ni(dmit)_2]^-$, and $[Ami]^+[Ni(dmit)_2]^-$ are abbreviated as **1**, **2**, **3**, **4**, and **5**, respectively (Chart 1).

Experimental

Materials. $(Bu_4N)[Ni(dmit)_2]$ was synthesized according to the literature.[30] 3-Carboxy-1-methylpyridinium hydrochloride was supplied by Kanto Chemical. 3-Benzoyl-1-methylpyridinium iodide, 3-acetyl-1-methylpyridinium iodide, 3-methoxycarbonyl-1-methylpyridinium iodide, and 3-aminocarbonyl-1-methylpyridinium iodide were prepared by a similar procedure as follows; pyridine at 3-position by the corresponding substituent (20 mmol) and methyl iodide (40 mmol) were stirred in acetone (25 mL) for a few minutes. The resultant crude solid was filtered and washed several times with acetone and Et_2O to obtain the derivative of each 1-methylpyridinium iodide. The crude products were used in the second reaction without further purification, and also all reagents including 3-carboxy-1-methylpyridinium hydrochloride were of reagent grade and used without further purification.

Synthesis of (Ben)[Ni(dmit)$_2$] (1). Single crystals of **1** were prepared by cation exchange and slow interdiffusion of an acetonitrile solution (25 mL) of $(Bu_4N)[Ni(dmit)_2]$ (0.05 mol) and a chloroform/methanol (15:1) solution (45 mL) of (Ben)I (0.1 mol) for several days at room temperature. Anal. Found: C, 34.91; H, 1.56; N, 2.11%. Calcd for $C_{19}H_{12}NNiOS_{10}$: C, 35.12; H, 1.86; N, 2.15%. IR (KBr, cm^{-1}): 3077 (w and br), 1657 (m, C=O), 1332 (s, C=C), 1061 (s, C=S).

Syntheses of (Ace)[Ni(dmit)$_2$] (2), (Met)[Ni(dmit)$_2$] (3), (Car)[Ni(dmit)$_2$] (4), (Ami)[Ni(dmit)$_2$] (5). Single crystals of **2**, **3**, **4**, and **5** were prepared in a similar way to **1** using (Ace)I (0.1 mmol), (Met)I (0.1 mmol), (Car)Cl (0.5 mmol), and (Ami)I (0.1 mmol), respectively, instead of (Ben)I. **2**; Anal. Found: C, 28.81; H, 1.42; N, 2.34%. Calcd for $C_{14}H_{10}NNiOS_{10}$: C, 28.61; H, 1.71; N, 2.38%. IR (KBr, cm^{-1}): 3077 (w), 1698 (m, C=O), 1342 (m, C=C), 1067 (m and br, C=S). **3**; Anal. Found: C, 28.25; H, 1.35; N, 2.29%. Calcd for $C_{14}H_{10}NNiO_2S_{10}$: C, 27.85; H, 1.66; N, 2.32%. IR (KBr, cm^{-1}): 3071 (w), 1718 (m, C=O), 1338 (s, C=C), 1064 (s and br, C=S). **4**; Anal. Found: C, 26.66; H, 0.97; N, 2.38%. Calcd for $C_{13}H_8NNiO_2S_{10}$: C, 26.48; H, 1.36; N, 2.37%. IR (KBr, cm^{-1}): 3857 (w), 3674 (w and br), 1725 (m, C=O), 1328 (s, C=C), 1257 (s), 1183 (m and br), 1064 (s), 1040 (s), 1023(s), 918 (s). **5**; Anal. Found: C, 26.51; H, 1.15; N, 4.58%. Calcd for $C_{13}H_9N_2NiOS_{10}$: C, 26.52; H, 1.54; N, 4.76%. IR (KBr, cm^{-1}): 3437 (w), 3315 (w), 3084 (w and br), 1688 (m, C=O), 1393 (m), 1345 (m, C=C), 1121 (m), 1057 (s, C=S).

X-ray Crystallography. A single crystal was mounted on a glass capillary. Intensity data were collected at 300(1) K by a Bruker AXS SMART diffractometer equipped with a CCD area detector and Mo Kα ($\lambda = 0.71073$ Å) radiation. The structures of **1**–**5** were solved and refined with SHELX-97[31] using direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically by the full-matrix least-square method. Some hydrogen atoms were found from experimental data directly, and their position and isotropic thermal parameters were refined. Selected crystallographic data are summarized in Table 1. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: Deposit numbers CCDC-665665–665661 for compounds **1**–**5**, 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, U.K.; FAX: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Measurements. IR spectra (KBr pellets) were measured with a JASCO FT/IR-410 spectrophotometer. Elemental analyses were performed with a Perkin-Elmer 2400II CHN analyzer. Conductivity measurements were carried out at ambient pressure using a two-probe ac impedance method. Electrical contacts were prepared using gold paste to attach 0.1 mmϕ gold wires (The Nilaco CORPORATION) to the crystals.

Results and Discussion

Structure of the Anions. ORTEP plots with atomic numbering scheme of all compounds **1**–**5** are given in Figure 1. There was one crystallographically independent $Ni(dmit)_2$ ion and one counter cation within an asymmetric unit. $[Ni(dmit)_2]$ in each crystal was almost planar (maximum deviations from the least-square plane: **1**, 0.1585(8) Å [S(2)]; **2**, 0.3981(34) Å [S(5)]; **3**, 0.879(13) Å [S(7)]; **4**, 0.1027(10) Å [S(6)]; and **5**, 0.3318(9) Å [S(7)]). The cation:anion ratios were 1:1 giving the $Ni(dmit)_2$ unit a formal charge of −1. The selected bond lengths and angles are listed in Table 2. There were no significant differences in bond lengths and angles of $Ni(dmit)_2$ anion within an asymmetric unit, except for **4**. A strong band around 1350 cm^{-1} in IR spectra assigned as the C=C stretching band, was known to exhibit large shift depending on 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 $[Ni(dmit)_2]^{2-}$.[32] The results (1328–1345 cm^{-1}) showed that the $Ni(dmit)_2$ unit of all **1**–**5** was monovalent, consistent with the crystal data. Since space groups of **1**, **3**, and **5** were $P2(1)/c$ or $/n$, anions were orientated in two directions forming two different stacking structures, while for those of **2** and **4** adopting $P\bar{1}$, only a single type of stacking was present (Figure 2).

Crystal Structures of (Ben)[Ni(dmit)$_2$] (1), (Ace)[Ni(dmit)$_2$] (2), and (Met)[Ni(dmit)$_2$] (3). In Figure 2, intermolecular S···S contacts shorter than 3.70 Å,[33] the sum of van der Waals radii of S atoms, are shown by dashed lines (Table 3). The crystal structure of **3** differed from the already reported structure.[25] The exact reason of the crystal polymorph is uncertain, but differences in the solvent used during crystal formation and the applied crystallization technique could be

Table 1. Crystallographic Data of Complex Salts **1**–**5**

		1	**2**	**3**	**4**	**5**
Formula		$C_{19}H_{12}NNiOS_{10}$	$C_{14}H_{10}NNiOS_{10}$	$C_{14}H_{10}NNiO_2S_{10}$	$C_{13}H_8NNiO_2S_{10}$	$C_{13}H_9N_2NiOS_{10}$
Fw		649.61	587.54	603.54	589.51	588.53
Crystal system		Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group		$P2(1)/n$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$
Unit cell	a/Å	12.4854(10)	7.494(2)	11.649(7)	7.5505(8)	6.7640(6)
	b/Å	12.3668(10)	12.034(4)	26.144(7)	11.5469(12)	45.244(4)
	c/Å	16.3463(14)	12.526(4)	7.694(7)	13.5068(14)	7.4079(6)
	α/degree		77.410(3)		105.623(2)	
	β/degree	104.1010(10)	80.381(6)	105.882(7)	99.563(2)	113.5830(10)
	γ/degree		82.180(6)		105.707(2)	
Volume/Å^3		2447.9(3)	1081.1(6)	2253.7(14)	1054.82(19)	2077.7(3)
Z		4	2	4	2	4
δ_{calcd}/Mg m^{-3}		1.763	1.805	1.779	1.856	1.881
μ/mm^{-1}		1.662	1.870	1.800	1.921	1.948
$F(000)$		1316	594	1220	594	1188
GOF[a)]		0.929	1.099	0.927	1.071	1.077
Final R	R_1[b)]	0.0378	0.0836	0.0374	0.0378	0.0379
indices [$I > 2\sigma(I)$]	wR_2[c)]	0.0552	0.1029	0.0698	0.0498	0.0482
R indices	R_1[b)]	0.0734	0.2593	0.0814	0.1011	0.0918
(all data)	wR_2[c)]	0.0788	0.2698	0.1260	0.1204	0.0953

a) Goodness-of-fit on F^2. b) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. c) $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

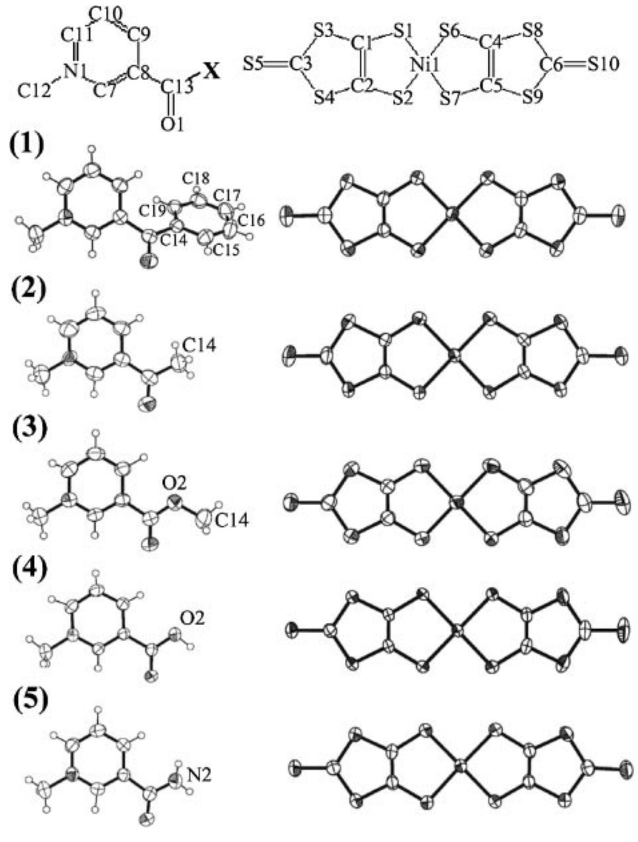


Figure 1. ORTEP III views of **1**–**5**, showing 50% probability ellipsoids with atom numbering scheme.

responsible.[34] Since S···S contacts did not occur in the direction of the b axis, anions formed a knit fabric-like structure possessing a two-dimensional S···S network along a and c axes (Figure 2(3)). The average interplanar distances between anion and cation of **3** was ca. 3.53 Å. However, cations were found to form centrosymmetrically associated dimers by two types of weak C(sp^2 and sp^3)–H···O hydrogen bonds, which were also present in the polymorph (Figure 3(3)).[25] Although the crystallization technique of this study, i.e., inter-diffusion, was different from that in Ref. 25, i.e., solvent evaporation, dimer of the same structure was present. Thus, this fact indicates the high stability of the dimeric structure shown in Figure 3(3).

Ace ions also formed similar centrosymmetrically associated dimers. The geometric parameters listed in Table 4 satisfied the following criteria reported for general C–H···O hydrogen bonding, i.e., C···O and H···O distances being 3.0–4.0 and 2.4–3.0 Å, respectively.[35–37] Also, anions of **2** formed a zig-zag sheet via S···S contacts between neighboring anions along b and c axes (Figure 2(2) and Table 3), and further S···S contacts along a axis were present between the sheets. Therefore these S···S contacts form a three-dimensional S···S network. The average interplanar distance between anion and cation of **2** were ca. 3.58 Å, slightly longer than that of **3**.

Furthermore, anions of **1** formed a deeply folded zig-zag structure like screen via S···S contacts between neighboring anions along a and c axes (Figure 2(1) and Table 3). There were also many S···S contacts between the sheets along the b axis. Consequently, S···S contacts in **1** also formed a three-dimensional network. The average interplanar distances between anion and the nearest pyridinium ring of the cation was ca. 3.50 Å. Unexpectedly, it was found that Ben cations also formed centrosymmetrically associated dimers similar to Met and Ace. Due to the bulkiness of the phenyl group, we expected a characteristic aggregation structure made by π···π stacking involving phenyl groups. The common structural feature of cation dimers led us to conclude that weak C(sp^2 and sp^3)–H···O hydrogen bonds effectively functioned to form dimer

Table 2. Selected Geometric Parameters

		1	**2**	**3**	**4**	**5**
Ni–S distance/Å		2.1551(7)–2.1678(7)	2.148(19)–2.1548(19)	2.1581(13)–2.1647(13)	2.1580(8)–2.1674(19)	2.1581(8)–2.1698(8)
cis-S–Ni–S angles/degree		86–93	86–94	87–93	87–93	86–93
Dihedral angle[a)]/degree		5⁽²⁾	9⁽¹⁾	2⁽¹⁾	8⁽¹⁾	3⁽³⁾
Dihedral angle between two ligands/degree		5	9	3	5	12
C=O distance/Å	C13=O1	1.215(3)	1.207(9)	1.200(5)	1.230(4)	1.211(4)
Terminal C=S distances/Å	C3=S5	1.634(3)	1.630(7)	1.634(4)	1.646(3)	1.640(3)
	C6=S10	1.642(3)	1.648(7)	1.634(4)	1.647(4)	1.632(3)

a) Dihedral angle between anion and counter cation of (1) x, y, z; (2) $x, 1/2 - y, -1/2 + z$; (3) $1/2 + x, 3/2 - y, 1/2 + z$.

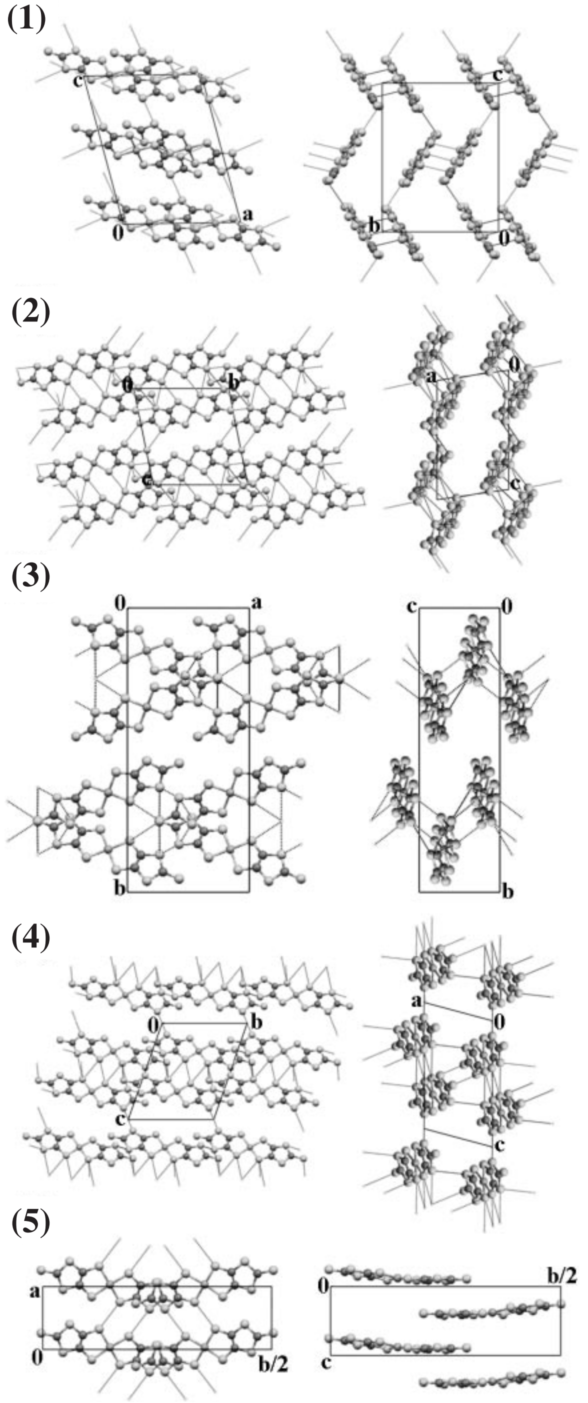


Figure 2. Crystal packing of [Ni(dmit)$_2$] anions in **1**–**5** viewed along two different directions; Dashed lines indicate the short S···S contacts.

(Figures 3(1)–3(3)). In addition, the dihedral angle between the pyridinium ring and phenyl group of a cation in **1** was 52.2°, while inter-planar dihedral angles between anion and neighboring cation were 5.04° for pyridinium ring, and 37.52° for phenyl ring. The fact that the positively charged pyridium ring preferably aligned parallel to the negatively charged anions, indicates the presence of Coulombic interaction between them.

Crystal Structure of (Car)[Ni(dmit)$_2$] (4) and (Ami)[Ni(dmit)$_2$] (5). Although the anions of **4** are similarly arranged

Table 3. Distances (Å) of S···S Contacts in **1**–**5**

1	S2···S9$^{a)}$	3.5658(10)	S3···S9$^{b)}$	3.3811(10)
	S4···S8$^{c)}$	3.5653(11)	S7···S7$^{a)}$	3.5142(14)
2	S3···S5$^{d)}$	3.595(4)	S4···S7$^{e)}$	3.550(3)
	S4···S8$^{f)}$	3.480(3)	S4···S9$^{e)}$	3.576(3)
	S4···S10$^{f)}$	3.540(4)	S9···S9$^{g)}$	3.521(5)
3	S3···S4$^{h)}$	3.5392(18)	S3···S9$^{i)}$	3.4737(19)
	S5···S7$^{j)}$	3.5704(17)	S5···S9$^{i)}$	3.671(2)
4	S1···S6$^{k)}$	3.5894(11)	S1···S5$^{l)}$	3.6207(13)
	S1···S5$^{k)}$	3.6530(15)	S4···S8$^{m)}$	3.6211(14)
	S6···S6$^{k)}$	3.4667(16)	S9···S9$^{n)}$	3.4402(19)
5	S1···S7$^{i)}$	3.6016(11)	S6···S9$^{i)}$	3.6433(11)

Symmetry codes: a) $2 - x, 2 - y, 2 - z$; b) $-1 + x, y, z$; c) $-1/2 + x, 3/2 - y, 1/2 + z$; d) $-x, 2 - y, 1 - z$; e) $-x, 1 - y, 2 - z$; f) $x, 1 + y, z$; g) $1 - x, -y, 2 - z$; h) $x, 1/2 - y, 1/2 + z$; i) $1 + x, y, z$; j) $1 + x, 1/2 - y, 1/2 + z$; k) $1 - x, 1 - y, 1 - z$; l) $-x, -y, 1 - z$; m) $-1 + x, -1 + y, z$; n) $1 - x, 2 - y, 2 - z$.

Table 4. Geometries (Å, degree) of C–H···O and O–H···O Hydrogen Bonds

	D–H···A	D···H	H···A	D···A	(D–H···A)
1	C7–H7···O1$^{a)}$	0.93	2.37	3.240(3)	155
	C12–H12C···O1$^{a)}$	0.96	2.83	3.340(4)	114
2	C7–H7···O1$^{b)}$	0.93	2.35	3.212(10)	155
	C12–H12A···O1$^{b)}$	0.96	2.44	3.251(12)	142
3	C7–H7···O1$^{c)}$	0.92	2.31	3.203(5)	164
	C12–H12A···O1$^{c)}$	0.96	2.71	3.538(6)	145
4	O2–H2···O1$^{d)}$	0.93	1.73	2.649(3)	172
5	C9–H9···O1$^{e)}$	0.95	2.94	3.296(4)	104
	C10–H10···O1$^{e)}$	0.98	2.31	3.014(4)	128

Symmetry code: a) $1 - x, 2 - y, 1 - z$; b) $1 - x, 1 - y, 1 - z$; c) $2 - x, -y, 2 - z$; d) $-x, -y, -z$; e) $-1 + x, y, z$.

as those in **2**, the arrangement of Car cations in **4** was totally different; i.e., zig-zag sheet in **2** and three-dimensional S···S network in **4** (Figures 2(2) and 2(4)). As for the arrangement of Car shown in Figure 3(4), Car formed centrosymmetrically associated dimers by O–H···O hydrogen bonds, often observed for carboxylic acids.[38,39] As reported in Refs. 38 and 39, the compounds possessing carboxylic acid has a strictly fixed orientation by strong O–H···O hydrogen bonding, and this hydrogen bond shows a remarkable tendency to form a characteristic structure in the crystal. Therefore, the strong O–H···O hydrogen bond between carboxylic groups predominated to change the crystal structure from those of **1**–**3**. However, we have already reported the crystal structure of Car cation and Ni(dmit)$_2$ anion in partially oxidized state.[40] In this report, we also observed that Car cations formed centrosymmetrically associated dimers similar to **1**–**3** by O–H···O and C–H···O hydrogen bonds.

In contrast to other complex salts, (Ami)[Ni(dmit)$_2$] (**5**) showed absolutely different crystal structure. As for the arrangements of cation and anion shown in Figures 2(5) and 3(5), two S···S contacts between neighboring anions occur along the *a* axis, thereby forming a one-dimensional S···S network. Two weak C(sp^2)–H···O hydrogen bonds at the carbonyl groups of Ami were found to connect the neighboring cations along the *a* axis, despite the Ami cation possessing an $-NH_2$ group which can form a much stronger N–H···O hydrogen bond. The reason why a weak C–H···O hydrogen bond was formed instead of a strong N–H···O hydrogen bond is still uncertain. However, according to the reported crystal structures of iodide, chloride, and picrate salts of Ami ion, N–H···O hydrogen bonding was present in iodide, but not in chloride.[41] In the case of picrate anion known as a strong electron acceptor,[42] Ami ion formed a N–H···O hydrogen bond with the OH group of picrate anion and also a very short C(sp^2)–H···O hydrogen bond. Selection between existing possible interactions is still an open question, but the one-dimensional chain structure of Ami observed here might be a stable arrangement when combined with Ni(dmit)$_2$ known as an acceptor molecule. It is noteworthy that the crystal structures of Ace (**2**), Car (**4**), and Ami (**5**) salts are totally different although their size and shape are similar. Planarity, electron density, strong hydrogen bond, etc., contribute to crystal structure, but the result shows that the weak C–H···O hydrogen bond also has a non-trivial influence.

Comparison with Similar Aggregation via C–H···O Hydrogen Bonds. When five crystal structures of **1**–**5** were thoroughly investigated, two structural characteristics for cation arrangement were observed in common. First, the oxygen atom of the carbonyl group sticks out to the near-side of the nitrogen in pyridinium ring. Second, pyridinium moieties and anions are almost parallel to each other. The dihedral angles between the plane of anion and the pyridinium ring of cation were 5.04, 9.15, 2.24, 7.83, and 3.37°, for **1**–**5**, respectively. However, [2-(2-methoxycarbonylethyl)-1-pyridinium][Ni(dmit)$_2$] complex salt reported previously also satisfied this second characteristic, despite the fact that the cation was not planar in geometry.[28] Therefore, this second characteristic is essential not of the planar cation, but rather of the positive-charge of pyridinium.

Cation bonding in **1**–**5** is shown in Figure 3. As described above, Ben, Ace, and, Met cations in their complex salt formed similar dimeric structure involving C–H···O hydrogen bonding, although three cations possessed substituents of different shape and size. IR spectral peaks assignable to C=O stretching were 1663, 1689, and 1729 cm^{-1} for Ben, Ace, and Met, which were also seen in their salts **1**–**3** (Table 2). The data clearly show that the C=O band is strengthened by electron donation (Table 5a). Furthermore, Table 5 shows that C(sp^2)–H···O tended to shorten as the electron-donating ability of substituents increased. This means that the increase in electron density of oxygen atom by electron donation strengthened the C(sp^2)–H···O hydrogen bond. These two results, formation of similar dimeric structure and systematic change in C(sp^2)–H···O distance, implied the non-negligible effect of weak hydrogen bonding on the crystal structure although Coulombic interaction still dominates.

C–H···S Interaction between Anions and Cation. Similar discussion may apply to C–H···S interaction between cation and anion.[43–48] The C(sp^3 and sp^2)–H···S interaction has rarely been discussed in the literature despite the widespread presence of sulfur in many synthetic and natural molecular architectures. However, some recent reports have discussed the role of C–H···S interaction and the influence of weak contacts on molecular packing of organic crystals.[49–53] Potrzebowski et al. reported the geometric criteria for the general C–H···S

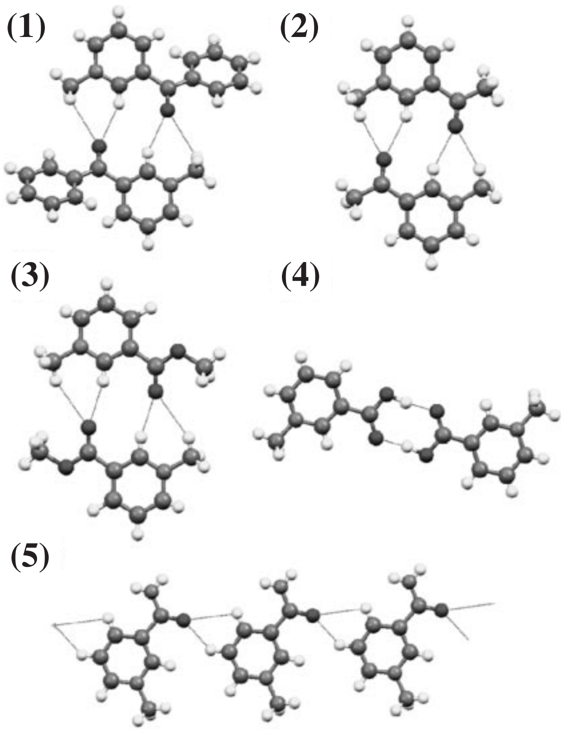
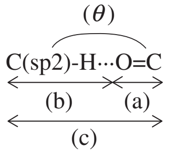


Figure 3. C–H···O and O–H···O hydrogen bonds between the cations in **1**–**5**, shown by dashed lines.

Table 5. Distances (Å) and Angles (degree) Related to C7–H7···O1=C13 Hydrogen Bond in the Centrosymmetrically Associated Dimers



		Ben	Ace	Met
(a)	O=C	1.215(3)	1.207(9)	1.200(5)
(b)	C···O	3.240(3)	3.212(10)	3.203(5)
(c)	C···C	4.343(4)	4.387(11)	4.379(6)
(θ)	C···O=C	155	155	164

interaction as follows; the C···S distances and C–H···S angles being 3.55–4.10 Å and 80–180°, respectively.[52] In Figure 4 and Table 6 are given the C–H···S interaction that matched the criteria. In all crystal structures, terminal sulfur atoms of the respective anions were placed near the protonated pyridinium and/or methyl groups. As reported by Miyazaki[43] and Veldhuizen et al.[44] considerable deviation from planarity in Ni(dmit)$_2$ units resulted not only from the S···S interactions but also from the N–H···S hydrogen bonds. The dihedral angle

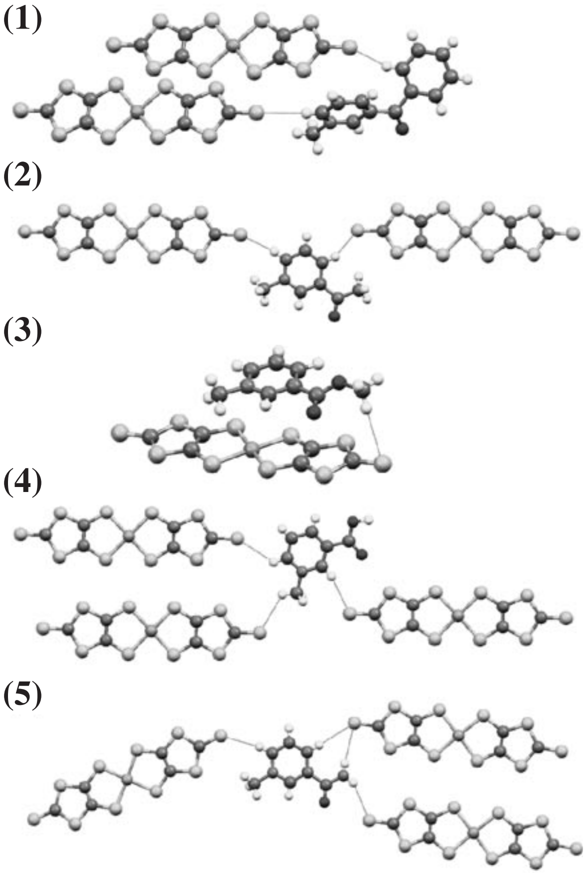


Figure 4. C–H···S and N–H···S hydrogen bonds between a cation and surrounding anions in **1**–**5**, shown by dashed lines.

Table 6. Geometries (Å, degree) of Hydrogen Bonds (Interactions) between Anions and Cation

	D–H···A	D···H	H···A	D···A	(D–H···A)	C=S
1	C19–H19···S5[a]	0.93	2.78	3.560(3)	142	1.634(3)
	C11–H11···S10[b]	0.93	2.81	3.733(3)	170	1.642(3)
2	C9–H9···S10[c]	0.93	2.88	3.602(9)	136	1.648(7)
	C11–H11···S10[d]	0.93	2.81	3.615(11)	146	1.648(7)
3	C14–H14C···S10[e]	0.96	2.98	3.935(6)	172	1.634(4)
4	C7–H7···S5[f]	0.91	2.83	3.710(3)	162	1.646(3)
	C12–H12A···S5[g]	0.96	2.96	3.612(3)	126	1.646(3)
	C11–H11···S10[h]	0.93	2.87	3.540(4)	130	1.647(4)
5	C9–H9···S5[i]	0.95	2.84	3.775(3)	169	1.640(3)
	C11–H11···S10	0.97	2.72	3.670(3)	169	1.632(3)
	N2–H2A···S5[j]	0.85	2.84	3.585(4)	147	1.640(3)
	N2–H2B···S5[i]	0.83	2.85	3.664(4)	170	1.640(3)

Symmetry codes: a) $1-x, 2-y, 2-z$; b) $-1+x, y, z$; c) $x, 1+y, z$; d) $1-x, -y, 2-z$; e) $1+x, y, 1+z$; f) $-x, -y, 1-z$; g) $x, 1+y, z$; h) $1-x, 2-y, 1-z$; i) $-x, 1/2+y, 3/2-z$; j) $1-x, 1/2+y, 3/2-z$.

between two dmit ligands in $[Ni(dmit)_2]$ were 4.84, 8.69, 2.51, 5.14, and 11.76°, for **1**–**5**, respectively. In the case of **5**, possessing N–H···S hydrogen bonds, apparent deviation was observed, as was the case in Refs. 43 and 44. Other salts exhibited smaller deviation, and no apparent relation between the length of terminal C=S and the C···S distance of possible C–H···S interaction could be found. Since other stronger interactions such as Coulombic interaction and O–H···O or C–H···O hydrogen bonding are already present, the effect of the C–H···S interaction, if present, should be limited to a certain extent.

Conductivity Measurements. The electric conductivities of single crystals of **1**–**5** measured at room temperature by two-probe alternating current were 1.00×10^{-6}, 1.10×10^{-6}, 2.86×10^{-6}, 9.77×10^{-6}, and $0.875 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$, respectively. Among highly conductive $[Ni(dmit)_2]^-$ salts, Reefman et al.[54] reported the (tmiz)$[Ni(dmit)_2]$ (tmiz = 1,2,3-trimethylimidazolium) salt featuring a cation that can be regarded as an intermediate between an open-shell and closed-shell cation. This compound showed a very high conductivity of 0.21 $\mathrm{S\,cm^{-1}}$ compared with other 1:1 $[Ni(dmit)_2]$ complex salts. Also, (MeQ)$[Ni(dmit)_2]$ (MeQ = *N*-methylquinolinium) was characterized by single-crystal X-ray analysis and exhibited a relatively high conductivity of $10^{-3}\,\mathrm{S\,cm^{-1}}$.[55] 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 $\pi\cdots\pi$ interaction between both cations and anions might be responsible for the high conductivity. However, $[Ni(dmit)_2]^-$ salts that exhibit high conductivity are comparatively rare, and their high conductivity may be attributed to the effective arrangement between anions and cations, as well as the formation of multi-dimensional S···S network between anions, or the partial auto-oxidation of anions which might be a cause of high conductivity. The conductivity of all complexes examined in this study were of the same level, and these complexes exhibited lower conductivity compared with the above rare cases. On the other hand, the crystal of *N*-ethylpyridinium cation,[56] whose structure was similar to cations examined in this study, with $Ni(dmit)_2$ formed crystal in a non-segregated manner, and the conductivity of this compound was $5 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$. Also, 3-(4- and 3-alkylpyridinium)-1,5-diphenylverdazyl radical cations with $Ni(dmit)_2$ formed crystal in a non-segregated manner, and the conductivity of these compounds were 10^{-4}–$10^{-6}\,\mathrm{S\,cm^{-1}}$.[57] Hence, we consider that the conductivities of **1**–**5** in this study were at the same level. As previously mentioned, the average distances between anion and cation of **1**–**5** were ca. 3.50, 3.58, 3.53, 3.41, and 3.53 Å, respectively. The fact that **4** has the closest contact and the highest conductivity compared with other complexes implies the presence of $\pi\cdots\pi$ interaction.

Conclusion

We have prepared five 1:1 complex salts composed of $[Ni(dmit)_2]^-$ anion and 3-X-1-methylpyridinium cations (X; benzoyl, acetyl, methoxycarbonyl, carbonyl, and, aminocarbonyl) to examine the importance of weak C–H···O hydrogen bonding on crystal structures of metal complex salts. We obtained preliminary results related to crystal engineering though improvement of conductivity was not achieved. Although the electrostatic interaction predominates and controls the crystal packing of the metal complex salts, the cations formed structurally similar dimers constructed by weak C–H···O hydrogen bonding, and the geometric parameters had correlation with electron-releasing ability of the substitutent linked to the carbonyl group (C=O). Although we need more consideration of crystallization parameters, the present results indicate that the pyridinium cations substituted at the 3-position by relatively weak electron-releasing substituent tends to form structurally-unique dimers by weak C–H···O hydrogen bonds in $[Ni(dmit)_2]^-$ salts.

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