

Systematic Change in Stacking Structure Induced by Alkyl Chains and Spectral Change Due to Hetero-Aggregation in $[Ni(dmit)_2]^-$ Salts of Methylene Blue Analogues

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A series of $[Ni(dmit)_2]^-$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato) salts of 3,7-bis(dialkylamino)phenothiazin-5-ium (alkyl = methyl (C1S), ethyl (C2S), propyl (C3S), and butyl (C4S)) together with those of 3,7-bis(diallylamino)-phenothiazin-5-ium (AS) and 3,7-bis(diethylamino)phenoxazin-5-ium (C2O) have been prepared and analyzed by X-ray crystal structural analysis and diffuse reflectance spectra. All complex salts formed stacking columns containing cations and anions. In the crystal structure of (C1S)$[Ni(dmit)_2]$, both C1S cations and $[Ni(dmit)_2]^-$ anions were found to form stacked dimers, and these dimers piled up alternately in columns. In the cases of (C2S)$[Ni(dmit)_2]$, (AS)$[Ni(dmit)_2]$, and (C2O)$[Ni(dmit)_2]$, cations and anions piled up alternately in the form of monomers. In the cases of (C3S)$[Ni(dmit)_2]$ and (C4S)$[Ni(dmit)_2]$, one anion was sandwiched between two cation dimers to form columns, and another anion layed between these columns. An absorption band appeared at 516–566 nm in the diffuse reflectance spectra, which originated from the absorption of blue cationic dyes, exhibited a large shift by the intermolecular interaction of cation–cation and cation–anion π-stacking. Compounds of (C1S)$[Ni(dmit)_2]$ and (C2O)$[Ni(dmit)_2]$ were found to behave as semiconductors, exhibiting room temperature conductivities of 3.8×10^{-6} and 4.5×10^{-7} S cm^{-1}, respectively.

Over the past decades, transition metal bis(dithiolate)-complexes have been subjects of great interest for studies on organic conductors and superconductors.[1] Seven molecular superconductors based on metal complexes of the dmit (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato) ligand have been discovered.[2–8] In general, the conduction paths in the $[M(dmit)_2]$ (M = Ni, Pd, and Pt) salts are formed by the overlapping of the orbitals of the sulfur atoms in the ligands. The counter cations used in the $[M(dmit)_2]$ salts can be closed shell cations as well as open shell ones.[9] The closed shell cations do not make any contribution to the conduction path, although their shapes and sizes play a crucial role in the arrangement of the anionic complexes, which will determine the electronic properties of the crystals. The closed shell cations that have been used so far are mostly of the tetraalkylammonium type. A few aromatic compounds have also been employed as the counter cations for the synthesis of $[Ni(dmit)_2]$ salts. The synthesis of (guanidinum)$[Ni(dmit)_2]_2$ showed that a planar cation in combination with $[Ni(dmit)_2]$ gives rise to short S–S interactions in three dimensions.[10] (Acridinium)$[Ni(dmit)_2]_3$ showed metallic conductivity behavior down to 4 K.[11] It was believed that not only the S–S contacts found between the $[Ni(dmit)_2]$ units, but also the interaction between the electronic systems of both the cations and the anions were responsible for its unusually high conductivity at room temperature.

Recently, we have combined cationic dyes with $[Ni(dmit)_2]^-$, with the intention to use the light absorbing nature of the dyes to modify the electronic state of $[Ni(dmit)_2]^-$. Thus, we started to search for cationic dyes that exhibit apparent spectral change when combined with $[Ni(dmit)_2]^-$. In the screening experiments, sulfur-containing cationic dyes were found to exhibit new absorption bands in the visible region. In this paper, the results of the structural and spectral analysis of $[Ni(dmit)_2]^-$ salts of sulfur-containing planar cations, methylene blue and its analogues, are reported. To our knowledge, this is the first report on the structural analysis of $[Ni(dmit)_2]^-$ salts with cationic dyes. The structure is compared with other reported salts of $[Ni(dmit)_2]^-$.

Experimental

Materials. 3,7-Bis(dialkylamino)phenothiazin-5-ium chloride (Methylene blue) and 3,7-bis(diethylamino)phenoxazin-5-ium chloride (Basic Blue 3) were supplied by Kanto Chemical and Aldrich, respectively. 4,5-Di(thiobenzoyl)-1,3-dithiole-2-thione and $(Bu_4N)[Ni(dmit)_2]$ were synthesized by the reported method.[12] Bromides of 3,7-bis(dialkylamino)phenothiazin-5-ium (alkyl = ethyl (C2S), propyl (C3S), and butyl (C4S)) and 3,7-bis(diallylamino)phenothiazin-5-ium ions (AS) were prepared by the reported method (Chart 1).[13] All other reagents were commercially available and used without further purifications.

Synthesis of (C1S)$[Ni(dmit)_2]$ (1). The preparation of a single crystal of **1** was performed by the cation-exchange method and slow inter-diffusion of acetonitrile solutions (50 mL) of $(Bu_4N)[Ni(dmit)_2]$ (0.1 mmol, 69 mg) and methylene blue (chloride trihydrate) (0.1 mmol, 37 mg) for 2 weeks at room temperature. Yield, 25 mg (33%). Anal. Found: C, 35.94; H, 2.27; N, 5.65%. Calcd for $C_{22}H_{18}N_3S_{11}Ni$: C, 35.91; H, 2.44; N, 5.70%. IR (KBr): 1353 cm^{-1} for $\nu_{(C=C)}$, 1054 cm^{-1} for $\nu_{(C=S)}$.

Synthesis of (C2S)$[Ni(dmit)_2]$ (2). 4,5-Di(thiobenzoyl)-1,3-dithiole-2-thione (920 mg, 2.25 mmol) was suspended in methanol (10 mL). Sodium methoxide in methanol (prepared from 322 mg

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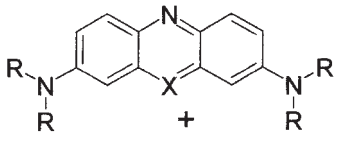
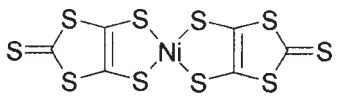


X = S, R = CH_3 (C1S)
X = S, R = C_2H_5 (C2S)
X = S, R = C_3H_7 (C3S)
X = S, R = C_4H_9 (C4S)
X = S, R = C_3H_5 (AS)
X = O, R = C_2H_5 (C2O)



$Ni(dmit)_2$

Chart 1.

of sodium in 7 mL of methanol) was added to the above mixture at room temperature for 20 min to give a dark red solution. To this solution, $NiCl_2 \cdot 6H_2O$ (238 mg, 1 mmol) was added. After 10 min, a solution of I_2 (127 mg, 1 mmol) and NaI (150 mg, 1 mmol) in methanol (20 mL) was added. After another 10 min, a solution of (C2S)Br (420 mg, 1 mmol) in methanol (20 mL) was added to the reaction mixture. The solution was stirred for 30 min and cooled in a refrigerator overnight. The resultant black crystal was collected by filtration, and purified by recrystallization using a mixed solvent of acetonitrile and benzene. Yield, 0.20 g (25%). Anal. Found: C, 39.55; H, 2.85; N, 5.21%. Calcd for $C_{26}H_{26}N_3S_{11}Ni$: C, 39.42; H, 3.31; N, 5.31%. IR (KBr): 1348 cm^{-1} for $\nu_{(C=C)}$, 1054 cm^{-1} for $\nu_{(C=S)}$.

Syntheses of (C3S)[Ni(dmit)$_2$] (3), (C4S)[Ni(dmit)$_2$] (4), (AS)[Ni(dmit)$_2$] (5), and (C2O)[Ni(dmit)$_2$] (6). **3**, **4**, **5**, and **6** were synthesized in a similar way to **2** using (C3S)Br (476 mg, 1 mmol), (C4S)Br (532 mg, 1 mmol), (AS)Br (468 mg, 1 mmol), and (C2O)Cl (408 mg, 1 mmol), respectively. **3**; Yield, 0.18 g (21%). Anal. Found: C, 42.79; H, 3.59; N, 4.88%. Calcd for $C_{30}H_{34}N_3S_{11}Ni$: C, 42.49; H, 4.04; N, 4.96%. IR (KBr): 1348 cm^{-1} for $\nu_{(C=C)}$, 1053 cm^{-1} for $\nu_{(C=S)}$. **4**; Yield, 0.15 g (17%). Anal. Found: C, 45.39; H, 4.34; N, 4.74%. Calcd for $C_{34}H_{42}N_3S_{11}Ni$: C, 45.16; H, 4.68; N, 4.64%. IR (KBr): 1350 cm^{-1} for $\nu_{(C=C)}$, 1051 cm^{-1} for $\nu_{(C=S)}$. **5**; Yield, 0.20 g (24%). Anal. Found: C, 42.81; H, 2.75; N, 4.91%. Calcd for $C_{30}H_{26}N_3S_{11}Ni$: C, 42.90; H, 3.12; N, 5.00%. IR (KBr): 1351 cm^{-1} for $\nu_{(C=C)}$, 1051 cm^{-1} for $\nu_{(C=S)}$. **6**; Yield, 0.25 g (32%). Anal. Found: C, 40.39; H, 3.48; N, 5.75%. Calcd for $C_{26}H_{26}N_3S_{10}ONi$: C, 40.25; H, 3.38; N, 5.42%. IR (KBr): 1349 cm^{-1} for $\nu_{(C=C)}$, 1050 cm^{-1} for $\nu_{(C=S)}$.

X-ray Crystallography. Single crystals were mounted on a glass capillary, transferred to a Bruker AXS SMART diffractometer equipped with a CCD area detector and Mo Kα ($\lambda = 0.71073$ Å) radiation, and centered in the beam at 297 K. The structures were solved and refined with SHELX-97[14] using the direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Crystal data are shown in Table 1. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-219246 and 263848–263852 for compounds **1**–**6**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Measurements. The IR spectra (KBr pellets) were measured by a JASCO FT/IR-410 spectrophotometer. The UV–vis–NIR spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer. The elemental analysis data were obtained with a Perkin-Elmer 2400II CHN Analyzer. Conductivity measurements were carried out at ambient pressure using the two-probe method. The compacted pellets were measured at room temperature.

Results and Discussion

Crystal Structural Change with Elongation of Alkyl Chains. The asymmetric unit of **1** with the labelling scheme

Table 1. Crystallographic Data of Complex Salts **1**–**6**

		1	**2**	**3**	**4**	**5**	**6**
Formula		$C_{22}H_{18}N_3NiS_{11}$	$C_{26}H_{26}N_3NiS_{11}$	$C_{30}H_{34}N_3NiS_{11}$	$C_{34}H_{42}N_3NiS_{11}$	$C_{30}H_{26}N_3NiS_{11}$	$C_{26}H_{26}N_3NiOS_{10}$
Fw		735.76	791.87	847.97	904.08	839.91	775.81
Crystal system		Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group		$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell	a/Å	14.2119(14)	14.1372(10)	10.7239(7)	11.8140(9)	9.0698(10)	9.2677(6)
	b/Å	14.2473(15)	9.3325(6)	13.1138(9)	13.1369(10)	29.862(3)	13.8210(9)
	c/Å	15.5314(16)	25.6111(18)	13.9313(10)	15.0025(11)	13.6833(15)	14.0040(9)
	α/deg	111.786(2)	90	91.698(2)	90.376(2)	90	107.5600(10)
	β/deg	102.174(2)	100.884(2)	100.471(2)	109.4440(10)	101.377(2)	100.8580(10)
	γ/deg	93.570(2)	90	91.208(2)	107.1780(10)	90	100.4800(10)
Volume	Å^3	2820.1(5)	3318.2(4)	1925.0(2)	2083.4(3)	3633.2(7)	1624.05(18)
Z		4	4	2	2	4	2
δ calcd	Mg/m^3	1.733	1.585	1.463	1.441	1.536	1.586
GOF[a]		1.018	0.681	0.742	0.868	0.887	0.907
Final R	$R1$[b]	0.0702	0.0402	0.0469	0.0404	0.0782	0.0387
indices [$I > 2\sigma(I)$]	$wR2$[c]	0.1534	0.0507	0.1151	0.0955	0.2049	0.0926
R indices	$R1$[b]	0.1087	0.1753	0.1683	0.0699	0.2012	0.0618
(all data)	$wR2$[c]	0.1748	0.0675	0.1458	0.1133	0.2684	0.1015

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

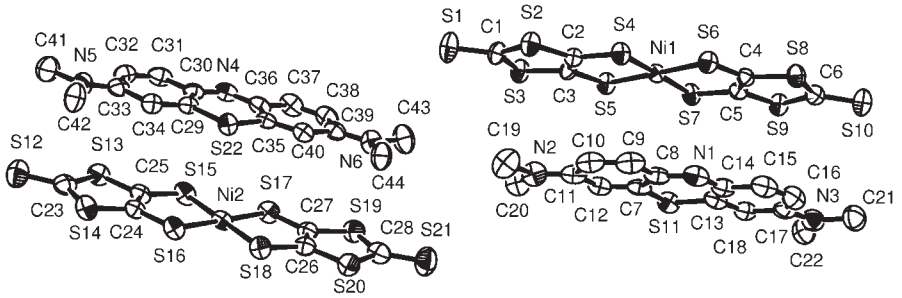


Fig. 1. Crystallographically independent units A (right) and B (left) of (C1S)[Ni(dmit)$_2$] (**1**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Table 2. Ni–S Distances of [Ni(dmit)$_2$]$^-$ and Dihedral Angles of Cation Rings

	1 (A unit)	**1** (B unit)	**2**	**3**	**4**
Ni–S distance/Å	2.163–2.175 (Ni1–S)	2.164–2.168 (Ni2–S)	2.148–2.174	2.160–2.164	2.156–2.164
Dihedral angle/deg	1.17	2.38	2.33	8.42	11.26

is depicted in Fig. 1. In the case of complex salts of *N*-methylquinolinium[15] or acridinium,[11] the NiS_4 coordination geometry of [Ni(dmit)$_2$]$^-$ was slightly distorted from square-planar toward a tetrahedral configuration. However, in the case of C1S salt, [Ni(dmit)$_2$]$^-$ was essentially planar. There were two independent molecular units, namely A and B units, of (C1S)[Ni(dmit)$_2$] in the crystal, but there were no significant differences in the bond lengths or angles among the two [Ni(dmit)$_2$]$^-$ anions of an asymmetric unit. The Ni–S distances were slightly larger than those (2.157–2.167 Å) of monovalent complexes.[16] The rings of the cations were also essentially planar. The C7–S11–C13 and C29–S22–C35 angles were 104.1(3) and 103.7(3)°, respectively. They deviated from the average angle of an aromatic ring, since the relatively large sulfur atom was involved. The structure was similar to that of methylene blue pentahydrate analyzed by Marr, III et al.[17]

In **2**, **3**, and **4**, the asymmetric units consist of two independent half anions and one cation. The NiS_4 coordination geometries of [Ni(dmit)$_2$]$^-$ were also essentially planar in all compounds, and the Ni–S distances, shown in Table 2, indicate that the formal charges of Ni(dmit)$_2$ were -1 in all of the compounds. The dihedral angles of the C10–C11–C17 and C11–C17–C16 plane in cation rings {exclusive of the dihedral angle of the C32–C33–C39 and C33–C39–C38 plane in the case of the B unit in **1**} in **1**, **2**, **3**, and **4** are given in Table 2. These data show that the cation is gradually twisted as the alkyl chain length elongates.

As is seen in Fig. 2, [Ni(dmit)$_2$]$^-$ and the cations of **1** form non-segregated stacks with the [Ni(dmit)$_2$]$^-$ dimers being sandwiched between the dimers of C1S cations, and vice versa. This structure is similar to that reported for the [Ni(dmit)$_2$]$^-$ salt of the 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium ion.[18] In both cases, the sizes of the cation and anion were almost the same, which is suitable for stacking. C1S cations in the dimer were oriented in opposite directions, maybe due to the following two reasons: The sulfur atoms possess a positive charge and the steric effect of amino methyl groups. This dimer structure is similar to that observed in methylene blue (thiocyanate).[19] There were two columns, A and B, shown

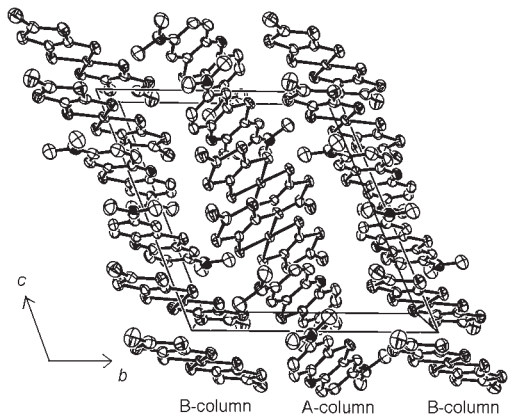


Fig. 2. Packing diagram of (C1S)[Ni(dmit)$_2$] (**1**). View down to *a*-axis. H atoms are omitted for clarity.

in Fig. 2, consisting of A and B units, respectively. In the A-column consisting of A units, [Ni(dmit)$_2$]$^-$ and C1S both formed dimers. This was also the case in the B-column, except for the slight difference in the stacking structures. A-column and B-column were not parallel, but were tilted by about 30° to each other. In this compound, five different inter-anion S–S contacts, shorter than the sum of the van der Waals radii, 3.654(2) Å (S1–S2 [$1-x$, $1-y$, $1-z$]), 3.544(3) Å (S2–S2 [$1-x$, $1-y$, $1-z$]), 3.637(2) Å (S3–S16 [$-1+x$, y, z]), 3.604(2) Å (S5–S16 [$-1+x$, y, z]), and 3.594(2) Å (S5–S18 [$-1+x$, y, z]), were found. Although S–S contacts between the dimers connect the neighboring columns electronically, intra-dimer interactions of [Ni(dmit)$_2$] were weak. Since the C1S cation is a π-conjugated cation and the cations tend to form a stacked dimer by π-electronic interaction, cation dimers become the components of the column.

In the crystal of **2**, the cation and anion monomers were piled up alternately to form a stacking column (Fig. 3). In the columns of **2**, a set of three ions, in which one anion was sandwiched by two cations, oriented in the same direction, but another anion was oriented in a direction differing by an angle of 45° to the set of three ions. A set of three ions and one anion

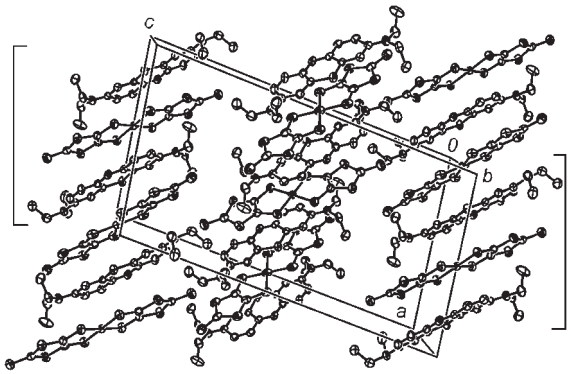


Fig. 3. Packing diagram of (C2S)[Ni(dmit)$_2$] (**2**). Sets of three ions are indicated by angled brackets. H atoms are omitted for clarity.

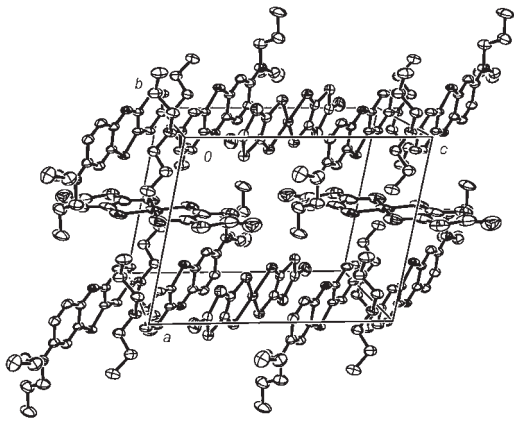


Fig. 4. Packing diagram of (C3S)[Ni(dmit)$_2$] (**3**). H atoms are omitted for clarity.

piled up in a column alternately in this manner. The shortest S–S contact was 3.670(2) Å (S1–S9 [$1-x$, $-1/2+y$, $1/2-z$]), indicating that the electronic interaction between $[Ni(dmit)_2]^-$ anions was weak. In **2**, the terminal methyl group of the C2S cation is found to deviate from the molecular plane, and sterically hinders the formation of the cation dimer. This disarrayed the stacking of the ions to form a crystal structure like **1**.

The stacking column arrangement of **3** and **4** are shown in Figs. 4 and 5, respectively. In the columns of these compounds, one anion was sandwiched between cation dimers, and another anion layed between these columns. In both columns of **3** and **4**, the sulfur atom of a cation had contact with the thiolato sulfur coordinated to the Ni atom. These inter-sulfur distances for **3** and **4** were 3.483(2) Å (S7–S11) and 3.661(1) Å (S7–S11 [$1-x$, $1-y$, $1-z$]), respectively. Although the complex located between the columns was essential planar, the thioxo groups at the ends deviated from the NiS_4 plane of the Ni complex. Since no marked interactions with other molecules were present, this distortion of the complex should be due to the packing arrangement. The inter-molecular S–S contacts of $[Ni(dmit)_2]^-$ were found in **4**, but not in **3**. Since the shortest contact distance is 3.690(1) Å (S4–S8), there is only a weak inter-molecular interaction. In the cases of **3** and **4**, the anion complexes are pushed out of the column to the vacant space produced between the columns by elongated alkyl groups.

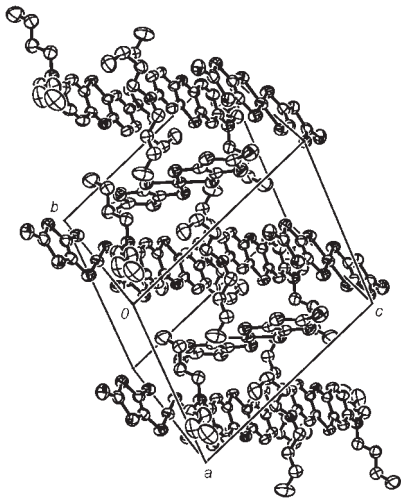


Fig. 5. Packing diagram of (C4S)[Ni(dmit)$_2$] (**4**). H atoms are omitted for clarity.

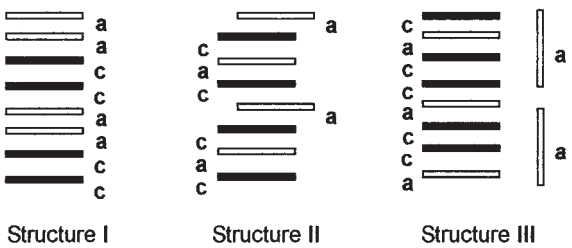


Fig. 6. Classification of stacking structures: **I** (**1**), **II** (**2**, **5**, and **6**), and **III** (**3** and **4**). Characters **a** and **c** represent the anion and cation, respectively.

The results show that the crystal structures of **1**–**4** can be classified into three categories: structure **I** for **1**, **II** for **2**, and **III** for **3** and **4**, as illustrated in Fig. 6. Structure **II** can be regarded as an intermediate structure between **I** and **III**, since half of the anions are largely displaced from stacking. In order to understand the relationship between the crystal structure and the substituted alkyl groups in detail, other cationic dyes, 3,7-bis(diallylamino)phenothiazin-5-ium (AS), the allyl substituted analogue of C1S, and 3,7-bis(diethylamino)phenoxazin-5-ium (C2O), the S to O substituted analogue of C2S, were used and investigated. The crystal structures of (AS)[Ni(dmit)$_2$] (**5**) and (C2O)[Ni(dmit)$_2$] (**6**), shown in Figs. 7 and 8, respectively, both adopted structure **II**. This result indicates that the substituted alkyl groups mainly control the crystal structure, and that the change in the electronic state of C2S and C2O did not affect the crystal packing. However, all anions are displaced from stacking in **5**. The allyl groups have three carbon atoms, but due to the planar nature of the double bond, the end vinyl group acts as a rigid group. Thus, the dynamic aspect of the allyl group is expected to resemble that of the ethyl group rather than that of the propyl group. This effect may have led the allyl group to exhibit an intermediate nature of the ethyl and propyl groups, and the crystal structure of **5** to take the largely distorted structure **II** instead of **III**. In **6**, however, the stacking structure closely resembled that of **2**, although one of the four ethyl groups in the C2O cation was disordered as shown in Fig. 9.

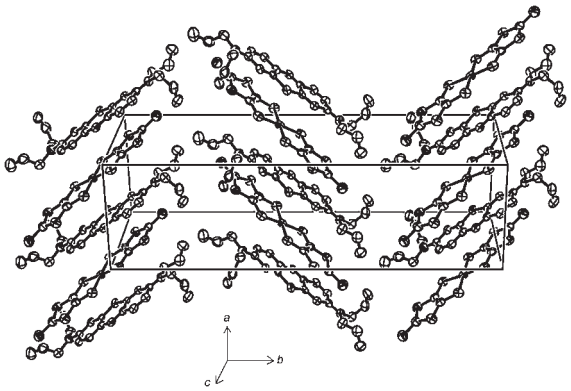


Fig. 7. Packing diagram of (AS)[Ni(dmit)$_2$] (**5**). H atoms are omitted for clarity.

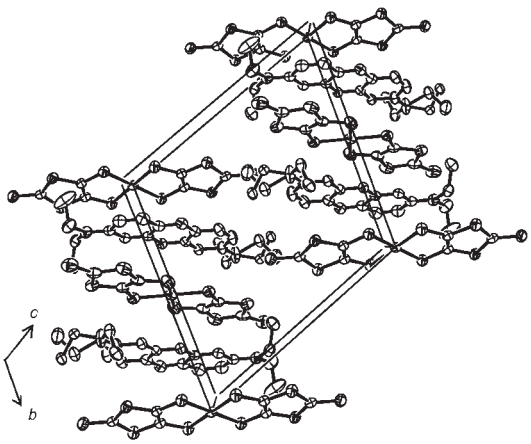


Fig. 8. Packing diagram of (C2O)[Ni(dmit)$_2$] (**6**). View down to *a*-axis. H atoms are omitted for clarity.

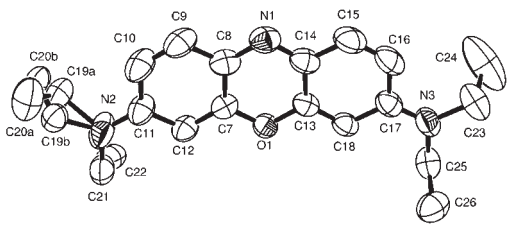


Fig. 9. ORTEP plot for C2O cation in **6**. H atoms are omitted for clarity. Disorder pairs of C19a–C20a and C19b–C20b are represented. Displacement ellipsoids are drawn at the 50% probability level.

UV–Vis–NIR Absorption and Diffuse Reflectance Spectroscopy. The UV–vis–NIR spectrum of **1** in DMF (1a) is given in Fig. 10. The intense absorption band at 666 nm ($\varepsilon = 65.5 \times 10^3$) is ascribed to the absorption of C1S, and the absorption bands at 398 nm ($\varepsilon = 13.0 \times 10^3$) and 1146 nm ($\varepsilon = 9.9 \times 10^3$) are ascribed to the absorption of [Ni(dmit)$_2$]$^-$.[20] Another absorption band at 627 nm of the charge-transfer bands should be present but is concealed by the intense absorption band of C1S. The absorption peaks of cationic dyes shifted to longer wavelengths with increasing alkyl chain length.

The diffuse reflectance spectrum of **1**, however, shows another broad band at around 538 nm. In the previous paper,[21]

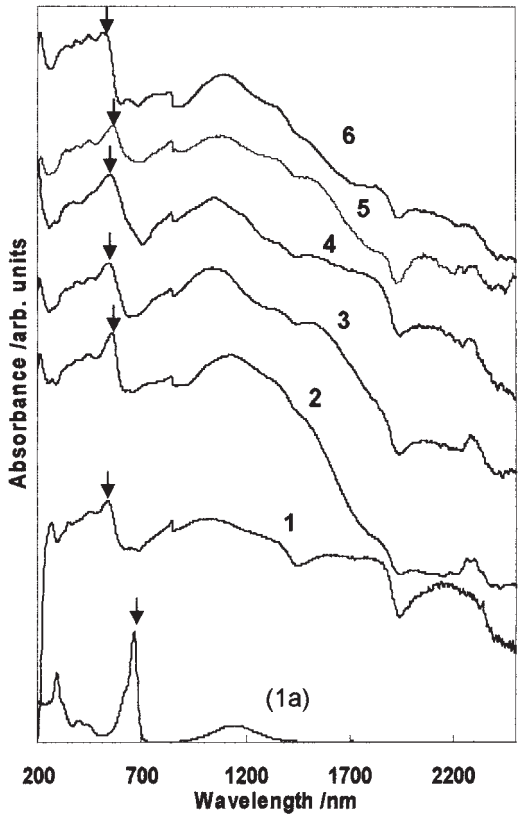


Fig. 10. Absorption spectrum of **1** in DMF (1a) and diffuse reflectance spectra of **1**–**6**. Peaks assigned to absorption of cationic dyes were indicated by arrow.

it is suggested that the visible absorption spectrum for C1S is complicated and highly dependent on the surrounding medium. C1S tends to aggregate and form dimers in solution. In aqueous solution, the spectrum of the C1S monomer was reported to have a maximum at 664 nm that shifts to 746 nm in strongly acidic conditions, while that of the dimer exhibited peaks at 605 and 685 nm, respectively.[21] Theoretically, the peak shift to shorter wavelengths is due to the face-to-face dimer and that of higher wavelengths is the result of end-to-end dimerization.[22] Therefore, the observed new absorption band is ascribed to the formation of the face-to-face dimer of C1S. The spectra of **2**–**6** also exhibited new absorption bands, but at different wavelengths. In Table 3, the shifts of the absorption bands of the crystals from that of the DMF solution are summarized. The data shows that the crystals adopting structures **I** and **III** (**1**, **3**, and **4**), where the dye cations form stacking dimers, exhibited large shifts. However, the large shifts observed for those of structure **II** should be caused by hetero-aggregation of cationic dyes and [Ni(dmit)$_2$]$^-$, as is reported for the porphyrin system.[23]

Conductivity Measurements. Compounds of **1** and **6** were found to behave as semiconductors, exhibiting a room temperature conductivity of 3.8×10^{-6} and 4.5×10^{-7} S cm^{-1}, respectively. Conductivities of **2**–**5** were less than 10^{-11} S cm^{-1}. Although the conduction path through S–S contacts of anions are not connected throughout the crystal, the conductivity of **1** was relatively high compared with those nor-

Table 3. Spectra Data of New Absorption Peaks in Diffuse Reflectance Spectra

Complex salt	**1**	**2**	**3**	**4**	**5**	**6**
λ_{max}[a)] in DMF/nm	664	666	671	675	660	652
ν_{max}[b)] in DMF/$\times 10^{-3}$ cm^{-1}	15.1	15.0	14.9	14.8	15.2	15.3
λ_{max} in solid state/nm	538	556	542	546	566	516
ν_{max} in solid state/$\times 10^{-3}$ cm^{-1}	18.6	18.0	18.5	18.3	17.7	19.4
$\Delta\nu$[c)]/$\times 10^{-3}$ cm^{-1}	3.5	3.0	3.6	3.5	2.5	4.1

a) Wavelength at absorption peak. b) Wavenumber at absorption peak. c) ν_{max} solid state $-$ ν_{max} in DMF.

mally found for Ni(dmit)$_2$ possessing a formal charge of -1. A contribution by π–π interactions between Ni(dmit)$_2$ and C1S, shown in Fig. 2, to electric conductivity may be present. In **6**, the presence of one-dimensional conduction paths through S–S contact should be the reason of conductivity.

References

1 P. Cassoux, L. Valade, in *Inorganic Materials*, ed. by D. W. Bruce, D. O'Hare, Wiley, Chichester, **1992**, Chap. 1, pp. 1–58.

2 L. Brossard, M. Ribault, L. Valade, P. Cassoux, *Physica B* **1986**, *143*, 378.

3 L. Brossard, M. Ribault, L. Valade, P. Cassoux, *J. Physiol. (Paris)* **1989**, *50*, 1521.

4 L. Brossard, H. Hurdequint, M. Ribault, L. Valade, J. P. Legros, P. Cassoux, *Synth. Met.* **1988**, *27*, B157.

5 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki, *Chem. Lett.* **1987**, 1819.

6 A. Kobayashi, R. Kato, A. Miyamoto, T. Naito, H. Kobayashi, R. A. Clark, A. E. Underhill, *Chem. Lett.* **1991**, 2163.

7 H. Kobayashi, K. Bun, T. Naito, R. Kato, A. Kobayashi, *Chem. Lett.* **1992**, 1909.

8 H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Kato, H. Kobayashi, H. Kuroda, *Chem. Lett.* **1993**, 1235.

9 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, *Coord. Chem. Rev.* **1991**, *110*, 155.

10 Y. S. J. Veldhuizen, N. Veldman, M. T. Lakin, A. L. Spek, P. M. Paulus, C. Faulmann, J. G. Haasnoot, W. J. A. Maaskant, J. Reedijk, *Inorg. Chim. Acta* **1996**, *245*, 27.

11 Y. S. J. Veldhuizen, J. G. Haasnoot, J. Reedijk, *Synth. Met.* **1997**, *86*, 1827.

12 G. Steimecke, H. J. Sieler, R. Kirmse, E. Hoyer, *Phosphorus Sulfur Relat. Elem.* **1979**, *7*, 49.

13 N. Leventis, M. Chen, C. Sotiriou-Leventis, *Tetrahedron* **1997**, *53*, 10083.

14 G. M. Sheldrick, *SHELXS-97 and SHELXL-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.

15 J. P. Cornelissen, E. J. Creyghton, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk, *Inorg. Chim. Acta* **1991**, *185*, 97.

16 D. Mentzafos, A. Hountas, *Acta Crystallogr. Sect. C* **1988**, *44*, 1550.

17 H. E. Marr, III, J. M. Stewart, *Acta Crystallogr. Sect. B* **1973**, *29*, 847.

18 I. Malfant, R. Andreu, P. G. Lacroix, C. Faulmann, P. Cassoux, *Inorg. Chem.* **1998**, *37*, 3361.

19 A. Kahn-Harari, R. E. Ballard, E. K. Norris, *Acta Crystallogr. Sect. B* **1973**, *29*, 1124.

20 G. Matsubayashi, K. Takahashi, T. Tanaka, *J. Chem. Soc., Dalton Trans.* **1988**, 967.

21 H. Nishikiori, S. Nagoya, N. Tanaka, A. Katsuki, T. Fujii, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 915.

22 K. Patil, R. Pawar, P. Talap, *Phys. Chem. Chem. Phys.* **2000**, *2*, 4313.

23 E. Ojadi, R. Selzer, H. Linschitz, *J. Am. Chem. Soc.* **1985**, *107*, 7783.