

Mixed-stack organic charge-transfer complexes with intercolumnar networks

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We report synthesis and examination of the electronic properties of an isomorphous series of mixed-stack organic charge-transfer complexes, composed of [bis(ethylenedithio)tetrathiafulvalene] (BEDT-TTF)-based electron donors and electron acceptors of halogen-substituted tetracyanoquinodimethanes (TCNQ's). Single crystals of (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ) were investigated as to their crystal structures, and optical and magnetic properties. The intermolecular overlaps between the stacked columns were comparable to the *face-to-face* overlap between the donor and the acceptor molecules inside the stacks. As seen from the optical and magnetic measurements, the (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(ClMeTCNQ) complexes were neutral, while the (BEDO-TTF)(Cl₂TCNQ) complex was found to be ionic. Among these complexes, anomalous magnetic properties were observed in the ionic complex of (BEDO-TTF)(Cl₂TCNQ). (BEDO-TTF)(Cl₂TCNQ) is a magnetic insulator with Curie-Weiss behavior in magnetic susceptibility followed by a sharp drop at around 120 K, which is in sharp contrast to conventional "spin-Peierls-type" nonmagnetic mixed-stack ionic compounds.

I. INTRODUCTION

Electron-donor molecules BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] and their analogues are well known since they afford a vast variety of two-dimensional (2D) organic metals and superconductors.¹ The combination of "side-by-side" and "face-to-face" intermolecular interaction, characteristic of BEDT-TTF's, brings about the construction of 2D layered structures and electronic band structures with a variety of BEDT-TTF-based cation radical salts.² Recently, we made use of this ability of the BEDT-TTF family in "donor-acceptor-type" organic conductors, and certain novel all-organic metals³ and superconductors⁴ were successfully obtained. A notable feature of the (BEDT-TTF)(TCNQ)-type conductors (TCNQ=tetracyanoquinodimethane) is that electronic instability in the one-dimensional (1D) TCNQ columns is suppressed by the 2D nature of the BEDT-TTF's. It is expected that applications for such a feature of BEDT-TTF's could be applied, not only in electrical conductors, but also in other organic solid-state systems such as magnetic substances. This paper focuses on BEDT-TTF-based mixed-stack charge-transfer (CT) complexes composed of alternating stacks of donor and acceptor molecules, which are classed as another important group of donor-acceptor-type CT complexes.

Mixed-stack CT complexes are known to be classified into two categories: neutral (N) solids, consisting of neutral donor (D) and acceptor (A) molecules, and ionic (I) solids, consisting of cation and anion radicals.⁵⁻⁷ The fact that, in a certain combination of D and A, the complexes exhibit collective electronic phenomena associated with valence instability, known as neutral-ionic phase transitions,⁸⁻¹⁰ has attracted considerable interest. To date, research into such mixed-stack compounds has been limited to those CT complexes which have a strong 1D nature along the DA stacks.¹¹⁻¹³ In these complexes, the ionic crystal lattices in-

volved with the $S = 1/2$ radical spins on each molecule have proved to be unstable against spin-Peierls (SP) type dimeric distortions, that leads to the formation of localized singlet DA pairs. One notable example is (TTF)(CA) (TTF=tetrathiafulvalene, CA=chloranil), which shows neutral-to-ionic phase transitions with variations in temperature. The change in molecular valence is accompanied by simultaneous SP-type dimerization in the ionic DA stacks. With the introduction of the BEDT-TTF family to the mixed-stack compounds, it is expected that the SP-type dimerization in the ionic DA stacks would be suppressed, as had occurred in the (BEDT-TTF)(TCNQ)-type conductors. This issue is vitally important to obtain compounds with various unconventional electronic properties; high (metal-like) electrical conductivity at the neutral-ionic border, or the magnetic NI transition which has a purely electronic character.^{14,15}

In this paper we report on the crystal structures and electronic properties of an isomorphous series of mixed-stack CT complexes composed of BEDT-TTF and its analogues as electron donor molecules. The substituted TCNQ's are used as electron acceptors, so as to systematically control their electron affinity with a combination of chlorine and methyl groups.¹⁶ The obtained crystals were characterized and found to have three typical charged states, namely, neutral (N), ionic (I) and NI boundary. Among these compounds, the ionic complex exhibits an anomalous feature in its magnetic susceptibility, which is in sharp contrast to the conventional mixed-stack CT complexes.

II. EXPERIMENT

The starting materials were obtained as follows: BEDT-TTF and Me₂TCNQ (2,5-dimethyl-TCNQ) were purchased from the *Tokyo Kasei Corporation*. BEDO-TTF [bis(ethylenedioxy)tetrathiafulvalene] was synthesized according to the literature provided.¹⁷ The substituted TCNQ's of

TABLE I. Crystal data and experimental details for structural analysis of (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ).

	(BEDT-TTF) -(Me ₂ TCNQ)	(BEDT-TTF) -(ClMeTCNQ)	(BEDO-TTF) -(Cl ₂ TCNQ)
Chemical formula	C ₂₄ S ₈ N ₄ H ₁₆	C ₂₃ S ₈ N ₄ H ₁₃ Cl ₁	C ₂₂ S ₄ O ₄ N ₄ H ₁₀ Cl ₂
Temp.	296 K	296 K	296 K
Formula wt.	616.90	637.32	593.49
<i>a</i> (Å)	7.5826(3)	7.6053(2)	7.265(8)
<i>b</i> (Å)	13.0362(5)	12.6687(5)	12.273(6)
<i>c</i> (Å)	13.5321(5)	13.7357(4)	13.435(6)
β (deg)	98.711(1)	99.3700(9)	105.22(5)
<i>V</i> (Å ³)	1322.20(8)	1305.77(7)	1155(1)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	2	2
<i>D</i> _{calc} (g/cm ³)	1.550	1.621	1.705
Dimensions (mm)	0.6×0.6×0.2	0.9×0.2×0.2	0.8×0.1×0.1
Radiation	Mo(K α)	Mo(K α)	Mo(K α)
Data collection	Imaging plate	Imaging plate	Diffractometer
Total reflection	3159	2976	2993
reflection used [$3\sigma(F_0) < F_0$]	2377	2380	2109
<i>R</i> ; <i>R</i> _w	0.038; 0.046	0.049; 0.061	0.089; 0.141
Weighting scheme	1/ σ_2	1/ σ_2	1/ σ_2
GOF	3.01	4.49	2.05

ClMeTCNQ (2-chloro-5-methyl-TCNQ) and Cl₂TCNQ (2,5-dichloro-TCNQ) were synthesized by modifying the synthetic method of 1,4-diiodo-2-chloro-5-methylbenzene and 1,4-diiodo-2,5-dichlorobenzene,^{18,19} respectively. The electron affinities of substituted TCNQ's depend mainly on the number of chlorine atoms, which are reported as 0.10 eV for Me₂TCNQ, 0.26 eV for ClMeTCNQ, and 0.41 eV for Cl₂TCNQ as measured by the electrochemical half-wave potentials.²⁰ BEDT-TTF and BEDO-TTF were purified by repeated processes of recrystallization, while Me₂TCNQ, ClMeTCNQ, and Cl₂TCNQ were purified by the combination of recrystallization and sublimation.

The CT complexes of (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ) were prepared by the reaction of stoichiometric quantities of the constituent molecules in chlorobenzene. Crystallization of the product was achieved by a controlled temperature slow cooling of the reaction solution down to 50 °C, and successively fixing at 50 °C for a few days. Hexagonal prisms were obtained with a maximum size of 5.0×1.0×0.4 mm³ in single crystals of (BEDT-TTF)(Me₂TCNQ), in which the crystal long axis is parallel to the crystallographic *a*-axis. For (BEDT-TTF)(ClMeTCNQ), elongated blocks were grown with a maximum size of 8.0×0.6×0.6 mm³ perpendicular to the (100), (011), and (01 $\bar{1}$) faces. For (BEDO-TTF)(Cl₂TCNQ), thin needles with a maximum size of 0.8×0.15×0.1 mm³ were obtained, in which the long axis of the crystal is parallel to the crystallographic *a* axis. We were unable to obtain crystals of mixed-stack-type CT complexes for the combination of BEDT-TTF and Cl₂TCNQ.

All the crystallographic data of the present complexes are summarized in Table I. The room temperature structure was determined for (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(ClMeTCNQ) with an imaging plate diffractometer

(Rigaku RAXIS) using Mo(K α) radiation. That of (BEDO-TTF)(Cl₂TCNQ) was determined with a four-axis diffractometer (RIGAKU AFC7R) using Mo(K α) radiation. The calculations were performed with the teXsan crystallographic software package from the *Molecular Structure Corporation*.²¹ All the crystallographic informations for these compounds were deposited to Cambridge Crystallographic Data Center.

The optical absorption spectra of these compounds were measured in a powdered sample in a KBr compaction pellet. The optical spectra were measured at room temperature with a grating monochromator (4000–30 000 cm⁻¹) and a Fourier-transform infrared spectrometer (500–5000 cm⁻¹). The magnetic measurements were carried out with a dc superconducting quantum interference device magnetometer. The diamagnetic component for the core electrons of the constituted molecules were subtracted using the magnetic susceptibility of the neutral donor and acceptor molecules.

III. RESULTS AND DISCUSSIONS

A. Crystal structures

The crystals of all the present complexes belong to the monoclinic system, space group *P*2₁/*n*. The packing modes for (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ) are almost identical, and consist of alternating stacks of donor and acceptor molecules along the *a* axes. Figure 1 shows the crystal structure of (BEDT-TTF)(ClMeTCNQ), (a) viewed along the *a* axis, and (b) viewed along the *b* axis, which is parallel to the mixed-stack column. The donor and the acceptor planes are almost parallel to each other inside the columns, forming a dihedral angle of about 11.5°, 6.55°, and 3.51° for (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-

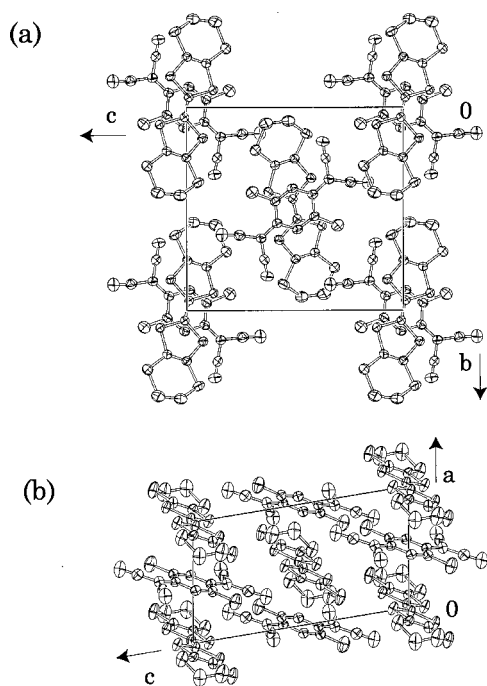


FIG. 1. Crystal structure of (BEDT-TTF)(ClMeTCNQ), (a) viewed along the a axis, which is parallel to the mixed-stacked column, and (b) viewed along the b axis.

TTF)(Cl₂TCNQ), respectively. The mean interplanar spacing between the donor and the acceptor is 3.79, 3.34, and 3.27 Å for (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ), respectively, which measurements are comparable to those of conventional mixed-stack CT complexes.

For all the complexes, the relative orientation of the molecular long axes of the donors and the acceptors is not parallel to each other, forming angles of about $\pi/3$ within the stacks, as seen in Fig. 1(a). This feature is characteristic of the mixed-stack CT complexes.²² Since the (HOMO) of the donors and the (LUMO) of the acceptors have opposite symmetry with respect to the inversion, the stabilization for CT interaction can be achieved by rotating the molecular long axes of the donor and the acceptor relative to each other. It indicates that the CT interaction between the donor and the acceptor molecules is much more sensitive to a subtle structural change in the mixed-stack compounds than in the

segregated-stack compounds. The substituent CH₃-CH₃ axis of Me₂TCNQ is parallel to the long axis of the donor in (BEDT-TTF)(Me₂TCNQ), while the substituent axes of the acceptors in (BEDO-TTF)(Cl₂TCNQ) and (BEDT-TTF)(ClMeTCNQ) form angles of $\pi/3$ with the long axis of the donors. In (BEDT-TTF)(ClMeTCNQ), the polar orientation of the CH₃-Cl axis in ClMeTCNQ is completely disordered, as is understood by the space group $P2_1/n$ of (BEDT-TTF)(ClMeTCNQ), in which the crystallographically independent atoms are half of those of the acceptor molecules.

As for the intercolumnar configuration, the nearest-neighbor column takes a position with a half sideways displacement along the long molecular axis of the donors to each other, in all the present complexes. In this respect, the intercolumnar side-by-side interaction was expected to be moderate in spite of the BEDT-TTF, as compared to the other types of (BEDT-TTF)(TCNQ)-based complexes: In (BEDT-TTF)(F₂TCNQ) [F₂TCNQ=2,5-difluoro-TCNQ], the nearest-neighbor column takes a position exactly at the side of the column, in which the side-by-side interaction between BEDT-TTF molecules dominates the CT interaction between the donors and the acceptors along the mixed-stack columns.²³ Intercolumnar S-S contact between the BEDT-TTF molecules is 3.464 Å in (BEDT-TTF)(ClMeTCNQ) and 3.299 Å in (BEDT-TTF)(Me₂TCNQ), which is shorter than twice the van der Waals radius (3.7 Å). Intercolumnar interactions comparable to those between D and A along the stacks, are afforded, as is discussed in the next section using overlap calculations.

B. Calculation of intermolecular overlap

The intermolecular overlap integrals were calculated on the basis of the extended Hückel molecular orbital method, for the HOMO of the donors and the LUMO of the acceptors, which is conventionally utilized and has been demonstrated to be effective by magnetoresistance oscillation measurements¹ as well as a scanning tunneling microscopy measurement.²⁴ The results are given in Table II for various combinations of neighboring molecules between the donor and the acceptor molecules. In the table, the third column indicates the crystallographic displacement vector connecting centers of the molecules for which the intermolecular overlaps are calculated. The overlap integrals between the

TABLE II. Intermolecular overlap integrals ($\times 10^{-3}$) for various combinations of neighboring molecules in (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ). The third column indicates the crystallographic displacement vector between centers of molecules used for calculation.

		Displacement vector ($\times 1/2$)	(BEDT-TTF) -(Me ₂ TCNQ)	(BEDT-TTF) -(ClMeTCNQ)	(BEDO-TTF) -(Cl ₂ TCNQ)
Intracolumn	D-A	[1, 0, 0]	7.38	9.5	0.74
	D-A	[0, 1, 1]	0.11	0.95	0.03
	D-A	[0, 1, -1]	2.87	0.3	0.43
Intercolumn	D-D	[1, 1, 1], [1, -1, 1]	0.81	1.5	0.068
	D-D	[1, -1, -1], [1, 1, -1]			
	A-A	[1, 1, 1], [1, -1, 1]	0.03	0.15	0.03
	A-A	[1, -1, -1], [1, 1, -1]			

TABLE III. Intermolecular overlap integrals ($\times 10^{-3}$) for various combinations of neighboring molecules in (TTF)(CA) and (BEDT-TTF)(F₂TCNQ).

		(TTF)(CA)	(BEDT-TTF) (F ₂ TCNQ)
Intracolumn	D-A	13.6	0.95
	D-A	0.25	0.55
Intercolumn	D-D	0.21	19.0
	A-A	0.02	0.48

donors and acceptors along the stacks are largest for all the present complexes. The result is consistent with the fundamental feature of mixed-stack CT compounds. In contrast, the intercolumnar overlaps are comparable with those along the stacks: The ratios of the largest intercolumnar overlap to the intracolumnar overlap are 39% in (BEDT-TTF)(Me₂TCNQ), 16% in (BEDT-TTF)(ClMeTCNQ), and 58% in (BEDO-TTF)(Cl₂TCNQ). The anisotropy of the intermolecular interactions is supposed to be small enough to suppress the spin-Peierls instability for all the present complexes.

In Table III, the intermolecular overlaps are shown for (TTF)(CA) and (BEDT-TTF)(F₂TCNQ), for comparison, both of which are other prototypical mixed-stack CT complexes with a strong anisotropic nature. As shown in the table, the *face-to-face* overlap along the stack is dominant in (TTF)(CA), while the *side-by-side* overlap perpendicular to the mixed-stack is predominant in (BEDT-TTF)(F₂TCNQ). It is noted that the result of (TTF)(CA) agrees well with the recent results of the *ab initio* calculations.²⁵ The relationship between the intracolumnar and intercolumnar interactions in the present complexes is in sharp contrast to those of (TTF)(CA) and (BEDT-TTF)(F₂TCNQ). In (BEDO-TTF)(Cl₂TCNQ), the values for the intermolecular overlap integrals are one order smaller than those of (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(ClMeTCNQ), as a whole. This is partly due to the fact that the coefficients of the oxygen atoms in the HOMO of the BEDO-TTF are smaller than those of the S_{out} atoms in the BEDT-TTF. We consider that the small *face-to-face* overlap along the stack is also associated with the complete ionicity ($\rho \sim 1$) of (BEDO-TTF)(Cl₂TCNQ), as discussed later.

C. Optical absorption spectra

The optical absorption spectra for these compounds are obtained in the range from 500 to 35 000 cm⁻¹. The results are shown in Fig. 2. The lowest electronic excitation, attributable to the CT band, is observed at around 5800 cm⁻¹ for (BEDT-TTF)(Me₂TCNQ), 4350 cm⁻¹ for (BEDT-TTF)(ClMeTCNQ), and 6290 cm⁻¹ for (BEDO-TTF)(Cl₂TCNQ), respectively, among which the CT-band energy is obtained to be lowest in (BEDT-TTF)(ClMeTCNQ). These CT-band energies are plotted against *I*-*A* (*I* and *A* are the ionization potential of the donors and the electron affinity of the acceptors, respectively) in Fig. 3 as postulated by Torrance *et al.*⁸ As seen in the figure, these complexes are located nearly at the bottom

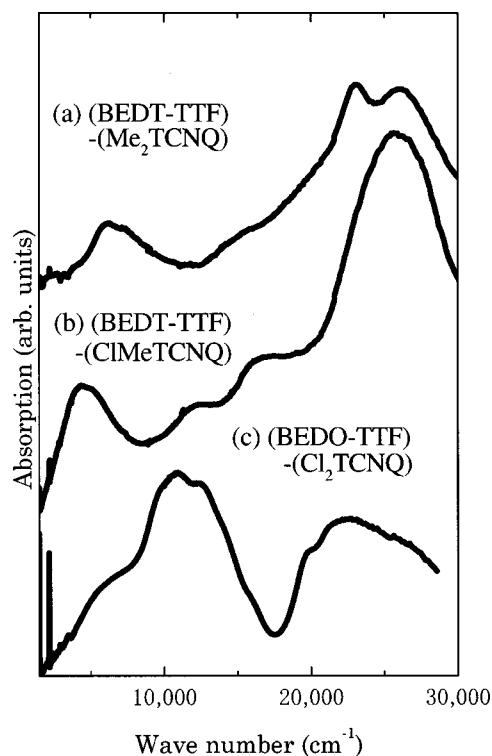


FIG. 2. Optical absorption spectra of (a) (BEDT-TTF)(Me₂TCNQ), (b) (BEDT-TTF)(ClMeTCNQ), and (c) (BEDO-TTF)(Cl₂TCNQ) at room temperature.

point of the V shape. Among the present complexes, (BEDT-TTF)(ClMeTCNQ) is closest to the border between the *N* and *I* states in the diagram. The results also indicate that (BEDO-TTF)(Cl₂TCNQ) is ionic, while (BEDT-TTF)(Me₂TCNQ) is a neutral complex.

Further evidence for the charged states of these complexes can be obtained from the intramolecular electronic

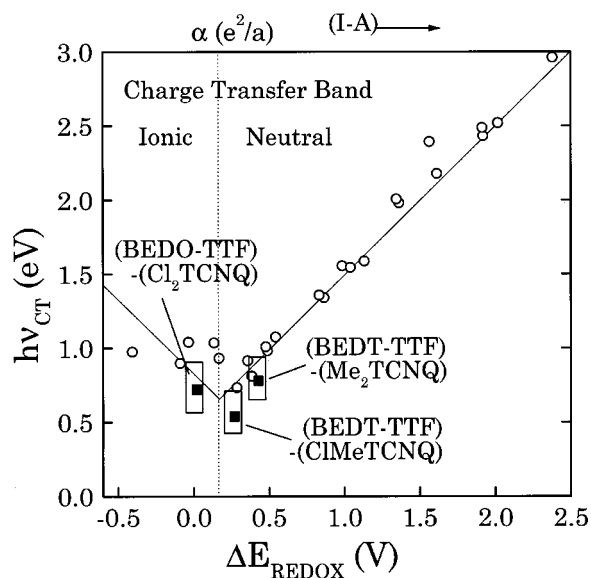


FIG. 3. Optical CT band energies are plotted against *I*-*A* for (BEDT-TTF)(Me₂TCNQ), (BEDT-TTF)(ClMeTCNQ), and (BEDO-TTF)(Cl₂TCNQ) in V-shape diagram for mixed-stack CT complexes proposed by Torrance *et al.* (Ref. 8). The open circles are reproduced from Fig. 1 of Ref. 8.

	BEDO-TTF ⁺¹	(BEDO-TTF) -(Cl ₂ TCNQ)	BEDO-TTF ⁰	BEDT-TTF ^{0.5}	(BEDT-TTF) -(CIME TCNQ)	(BEDT-TTF) -(Me ₂ TCNQ)	BEDT-TTF ⁰
a (C=C)	1.398 Å	1.399(6) Å	1.357 Å	1.370(7) Å	1.353(5) Å	1.341(5) Å	1.343(4) Å
b (C-S)	1.723 Å	1.720(3) Å	1.762 Å	1.735(6) Å	1.746(3) Å	1.750(3) Å	1.756(3) Å
c (S-C)	1.727 Å	1.732(3) Å	1.754 Å	1.749(6) Å	1.752(3) Å	1.750(3) Å	1.760(3) Å
d (C=C)	1.350 Å	1.344(4) Å	1.333 Å	1.345(7) Å	1.337(4) Å	1.348(4) Å	1.333(4) Å

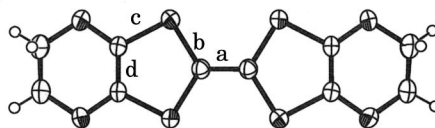


FIG. 4. Averaged four most central intramolecular bond lengths of BEDO-TTF and BEDT-TTF for present complexes. Those for neutral BEDO-TTF⁰ and ionic BEDO-TTF⁺¹, and BEDT-TTF⁰ and BEDT-TTF^{+1/2} are also shown for comparison.

excitation in the absorption spectra. From the results shown in Fig. 2, all the features of the intramolecular bands in (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CIME TCNQ) are similar, while the intramolecular bands of (BEDO-TTF)(Cl₂TCNQ) exhibit a nature which is considerably different from that observed in the other spectra. The following features are seen in the spectra: (1) In the visible range of the absorption spectra, the intramolecular band attributable to the HOMO-LUMO excitation of the donors and the acceptors is observed at around 23 000–27 000 cm⁻¹ in (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CIME TCNQ), while those of (BEDO-TTF)(Cl₂TCNQ) can be observed at a considerably lower energy of 19 000–25 000 cm⁻¹. Such kind of redshift of the intramolecular excitation is typical for ionic compounds. (2) In the near infrared range, an intense band can be observed at around 10 000–13 000 cm⁻¹ in (BEDO-TTF)(Cl₂TCNQ), which is attributable to the electronic excitation from the HOMO-1 to HOMO. This band is characteristic of BEDO-TTF⁺ radical cation as observed in (BEDO-TTF)I₃.²⁶ In (BEDT-TTF)(CIME TCNQ), an absorption band is also observed in this range, though the relative intensity is very weak. (3) In the midinfrared range, the relative intensity of the CT band is much smaller in (BEDO-TTF)(Cl₂TCNQ) than in (BEDT-TTF)(CIME TCNQ) and (BEDT-TTF)(Me₂TCNQ), indicating the weak CT interaction in (BEDO-TTF)(Cl₂TCNQ).

From these phenomena, we can conclude that both the (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CIME TCNQ) complexes are neutral solids at room temperature, while the (BEDO-TTF)(Cl₂TCNQ) complex is ionic. Although the polarized reflectivity spectra will be effective for detailed discussion, it is clear that in the absorption spectrum of (BEDO-TTF)(Cl₂TCNQ), the observation (2) indicates the nearly complete ionicity in (BEDO-TTF)(Cl₂TCNQ), while observation (3) indicates the weak CT interaction. From this point of view, it is found that crystals of (BEDO-TTF)(Cl₂TCNQ) are structurally stabilized mainly by the Madelung energy for ionic crystals,²⁷ and the contribution of CT interaction is fairly small.

D. Estimation of the degree of charge transfer

In the mixed-stack compounds, the CT interaction between the *D* and *A* molecules affords ground states with a partial charge transfer [$D^{+\rho}A^{-\rho}$ ($0 < \rho < 1$)], due to the hybridization between the neutral [D^0A^0] and the ionic

[D^+A^-] states, though they are classified as nominal “neutral” and nominal “ionic” compounds, in terms of the existing radical spins. The degree of CT (ρ) [$D^{+\rho}A^{-\rho}$] can be numerically estimated by the various geometric parameters as well as by the vibronic spectra for the constituent molecules. The left side of Fig. 4 shows the four most central intramolecular bond lengths of BEDO-TTF of (BEDO-TTF)(Cl₂TCNQ) with those for the neutral BEDO-TTF⁰ and the ionic BEDO-TTF⁺¹.²⁶ The comparison of the bond lengths clearly shows that the BEDO-TTF of (BEDO-TTF)(Cl₂TCNQ) is almost completely ionized, which is consistent with the optical spectra.

On the right side of Fig. 4, the four most central intramolecular bond lengths of BEDT-TTF for (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CIME TCNQ) can be seen, with those for neutral BEDT-TTF⁰ and BEDT-TTF^{+0.5}.^{28,29} For (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CIME TCNQ), we calculated our estimations (ρ) of BEDT-TTF by an empirical method suggested by Guineau *et al.*²⁸ which makes use of the relation ($\rho = 6.347 - 7.463\delta$), where [$\delta = (b+c) - (a+d)$]. The result is obtained as $\rho = 0.30$ for (BEDT-TTF)(Me₂TCNQ) and $\rho = 0.32$ for (BEDT-TTF)(CIME TCNQ).

Similar information can be also obtained from the frequency of C≡N stretching mode of acceptor molecules in vibronic spectra, shown in Fig. 5. If we extrapolate the linear dependence of the frequency of C≡N stretching mode in TCNQ to Me₂TCNQ and CIME TCNQ,³⁰ we can estimate the degree of CT as $\rho \sim 0.1$ for (BEDT-TTF)(Me₂TCNQ), $\rho \sim 0.5$ for (BEDT-TTF)(CIME TCNQ), though the result is somewhat different from the results as estimated by geometric parameters. In (BEDO-TTF)(Cl₂TCNQ), the main peak of the C≡N stretching mode is observed at lower frequency of the main peak of K(Cl₂TCNQ), though the peak structures seem to be different from those of the neutral and the K(Cl₂TCNQ). As it is impossible to avoid ambiguity completely in the present estimation, we can rationally estimate that the degree of charge transfer is $\rho = 0.1-0.3$ for (BEDT-TTF)(Me₂TCNQ), $\rho = 0.3-0.5$ for (BEDT-TTF)(CIME TCNQ), and $\rho \sim 1$ for (BEDO-TTF)(Cl₂TCNQ).

E. Magnetic properties

A striking feature in this series of complexes appears in the magnetic properties of the ionic compound. The spin susceptibilities of (BEDT-TTF)(CIME TCNQ) and (BEDO-

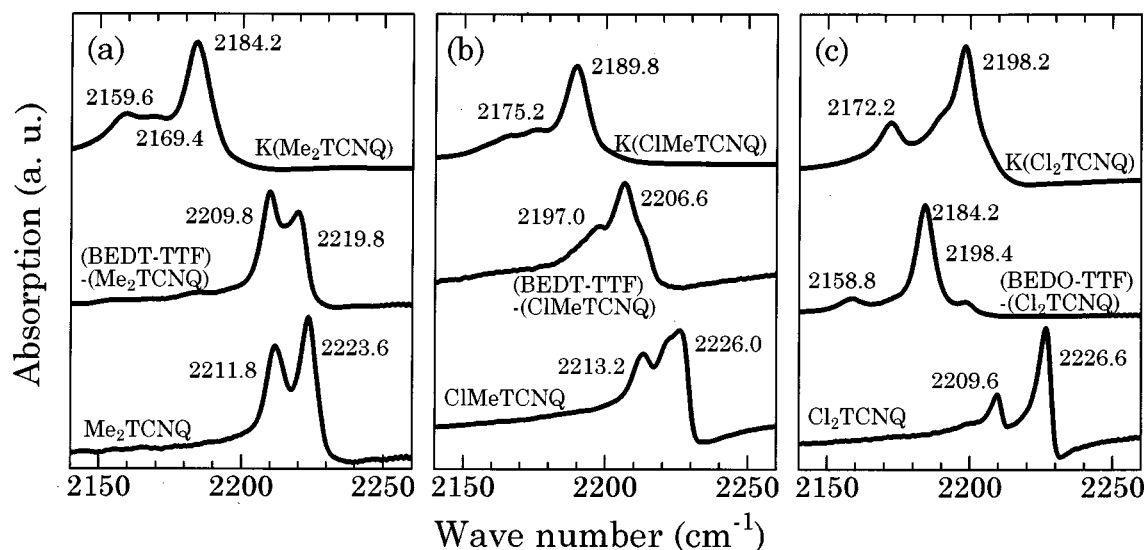


FIG. 5. Infrared vibronic spectra for C≡N stretching mode. (a) K(Me₂TCNQ), (BEDT-TTF)(Me₂TCNQ), and neutral Me₂TCNQ. (b) K(CiMeTCNQ), (BEDT-TTF)(CiMeTCNQ), and neutral CiMeTCNQ. (c) K(Cl₂TCNQ), (BEDO-TTF)(Cl₂TCNQ), and neutral Cl₂TCNQ.

TTF)(Cl₂TCNQ) are shown in Fig. 6(a). As seen in this figure, the susceptibility of (BEDT-TTF)(CiMeTCNQ) is fairly small, without showing any sign of magnetic anomaly.

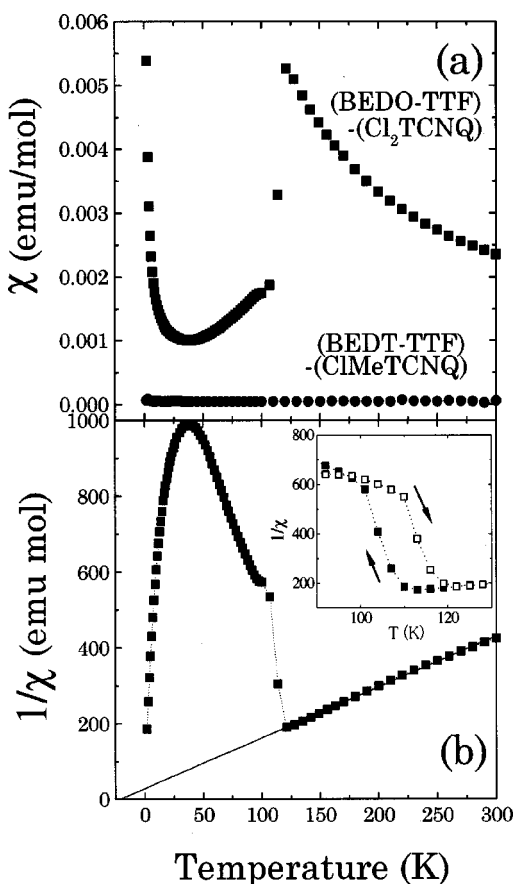


FIG. 6. (a) Temperature dependence of magnetic susceptibility for (BEDT-TTF)(CiMeTCNQ), shown by filled circles, and that for (BEDO-TTF)(Cl₂TCNQ) shown by filled squares. (b) $1/\chi$ plot against temperature for (BEDO-TTF)(Cl₂TCNQ). Inset shows the variation of magnetic susceptibility with increasing (open squares) and decreasing (filled squares) of temperature.

The magnetic susceptibility for (BEDT-TTF)(Me₂TCNQ) exhibits similar nonmagnetic behavior over the measured temperature range. The results imply that (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CiMeTCNQ) preserve their neutral states down to 4 K at ambient pressure. In contrast, (BEDO-TTF)(Cl₂TCNQ) exhibits peculiar paramagnetic behavior, where the magnetic susceptibility increases with decreasing temperature, followed by a sharp drop at 100–120 K.

Figure 6(b) shows the $1/\chi$ plot against temperature for (BEDO-TTF)(Cl₂TCNQ). The magnetic susceptibility at temperatures higher than 120 K roughly obeys the Curie-Weiss law ($C \sim 0.744$ emu K mol⁻¹, $\Theta \sim -21$ K). The estimated Curie constant corresponds to the spin density of approximately two Bohr magnetons per formula unit. The origin of the observed Curie-Weiss behavior in (BEDO-TTF)(Cl₂TCNQ) is ascribed to the radical 1/2 spins of the constituent donor and acceptor molecules, indicating that they have a strongly localized nature above 120 K. The observed exchange interaction of approximately $J \sim 20$ K is one order smaller than that of conventional mixed-stack ionic CT complexes ($J = 100$ – 1000 K).^{7,31} It is noted that as described in Sec. III D, an almost complete CT ($\rho \sim 1$) is observed in (BEDO-TTF)(Cl₂TCNQ), which offers a consistent picture for such a small exchange interaction, since the complete CT is achieved when the CT interaction between the donor and the acceptor molecules is considerably small along the stacks.

The localized behavior of magnetic susceptibility above 120 K is followed by a sharp drop at around 100–120 K. This magnetic anomaly shows a large hysteresis (8–10 K) against temperature, as shown in the inset of Fig. 6(b). This hysteretic change provides a clear evidence that the observed magnetic anomaly is a first-order phase transition, probably accompanied by lattice deformations. Below this sharp drop, the susceptibility decreases with temperature down to 35 K. The upturn below 35 K is attributed to the paramagnetic impurity with a spin density of 1–2.5 % per formula unit.³² All of the above features, particularly the magnetic anomaly

at around 120 K, are quite unique in comparison with the magnetic properties of the conventional mixed-stack ionic compounds. We conjecture that the origin of these peculiar features can be ascribed to the effect of the intercolumnar interaction by the BEDT-TTF analogues.

Prior to the discussion on the above observation, we would like to summarize briefly the magnetic properties of the conventional mixed-stack ionic complexes with one-dimensional structures.⁷ In such compounds, except for few exceptions,³³ both the strong intracolumnar interaction and the instability against dimeric lattice distortions have been believed to be the basis for understanding the magnetic properties. The suppressed magnetic susceptibility in the paramagnetic states has been understood in terms of the exchange interaction via the Bonner-Fischer mechanism, and the commonly observed nonmagnetic ground state is explained by the spin-Peierls-like dimerization. Magnetic properties of the (BEDO-TTF)(Cl₂TCNQ) form a striking contrast to the magnetic properties of these conventional ones, being suggestive of a new aspect of mixed-stack ionic CT compounds caused by an introduction of intercolumnar interactions.

To explain the magnetic anomaly at 100–120 K, there are four possible scenarios:

- (1) Valence change from high-temperature magnetic ionic states to nonmagnetic neutral states.
- (2) Dimeric lattice distortions below the magnetic anomaly which alternatively modulate the exchange interaction and cause a magnetic gap in the low-temperature phase.
- (3) The antiferromagnetic order at 100–120 K associated with structural change.
- (4) Another mechanism of susceptibility suppression with maintaining their regular stacks and without magnetic order.

In order to examine the above possibilities, we measured the infrared vibronic spectra, x-ray photographs, and electronic paramagnetic resonance (EPR) spectra below 100–120 K. We did not detect any changes of vibronic states such as frequency of C≡N and C=C stretching modes or activation of the optically forbidden (*a_g*) modes in the infrared spectra down to 20 K. Also, the x-ray photographs revealed that neither superlattice reflections nor change in the systematic absence of the Bragg reflections (space group *P2₁/n*) is observed above 95 K. These experimental results indicate that there is no sign of valence change or dimerization in the low temperature phase, excluding the possibilities numbered (1) and (2) above. In addition, the EPR experiments clarified that only intensity drops at 100–120 K, without any anomaly in the linewidth, indicating that the phase transition is not associated with magnetic ordering. All these considerations exclude the scenarios numbered (1)–(3), leading to model (4), where the transition at 100–120 K takes place while maintaining their regular stacks and without magnetic order.

For a further examination of the magnetic anomaly, we would like to present a discussion of the magnetic susceptibility of the low-temperature phase below 100–120 K, according to scenario (4). Figure 7 shows the comparison of experimental magnetic susceptibility vs temperature results with some calculated curves. A better fit is obtained by a

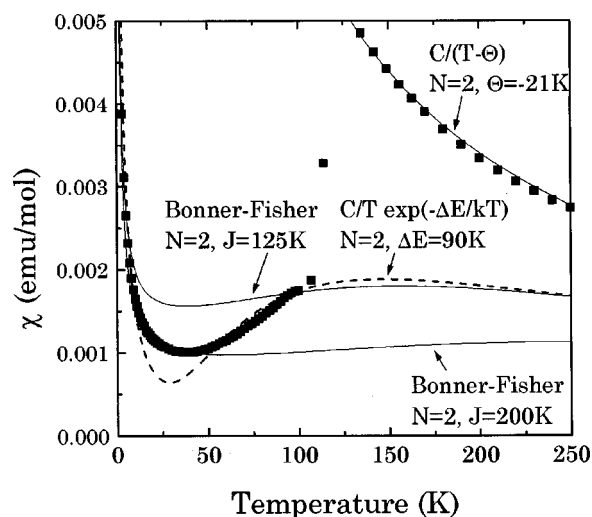


FIG. 7. Comparison of experimental magnetic susceptibility vs temperature results (filled squares) with some calculated curves; a dashed curve indicates a thermal-activation ($=CT^{-1}\exp(-\Delta E/kT)$; $\Delta E=90$ K) fit, and thin solid curves indicate Bonner-Fisher ($J=125$ K and $J=200$ K) fits, where two paramagnetic spins per formula unit with additional impurity Curie component are postulated.

thermal-activation [$CT^{-1}\exp(-\Delta E/kT)$] curve,⁶ (the curve is also known to be given by one-dimensional Ising model) shown by a dashed curve ($\Delta E=90$ K). However, we should keep in mind that we have no experimental evidence for the magnetic gap formation in this compound, as discussed above. We suggest that one possible explanation is a formation of pseudospingap due to short-ranged spin-Peierls-like fluctuations, as is frequently observed in the conducting CT complexes with strong one-dimensionality.³⁴

Another possibility is to ascribe the drastic change of the susceptibility to a variation of the exchange interaction, taking into account that the CT interaction between the donor and the acceptor molecules is very sensitive to a subtle change of the intracolumnar mixed-stack structures, as mentioned in the previous paragraph. Calculations, displayed by thin solid curves in Fig. 7, were made by a one-dimensional Heisenberg model for $J=125$ K and $J=200$ K (two paramagnetic spins per formula unit with additional impurity Curie component of 1%). As seen in this figure, it requires a large variation of the exchange interaction at 100–120 K by a factor of 6–15; simple calculations clearly indicate that J changes from $J\sim 20$ K in the high-temperature phase to $J\sim 300$ K [in the three-dimensional (Curie-Weiss) model], or to $J\sim 125$ K [in the one-dimensional (Bonner-Fisher) model], in the low-temperature phase. It is interesting to note that the obtained J values in the low-temperature phase are comparable to those of the conventional mixed-stack compounds. However, the agreement between the experiment and the Bonner-Fisher curves is still rather poor, as seen in Fig. 7. We think that it can also be rationalized by considering that the exchange interaction is temperature dependent in the low-temperature phase. Further theoretical and experimental investigations are necessary to achieve sufficient comprehension of the magnetic properties of (BEDO-TTF)(Cl₂TCNQ).

The above considerations lead us to conclude that the magnetic transition at 100–120 K is associated with struc-

tural change that suppresses the magnetic susceptibility drastically, while maintaining their regular stacks. This type of phase transition is unique to the mixed-stack ionic compounds with regular stack structures, which are realized in (BEDO-TTF)(Cl₂TCNQ) by an introduction of intercolumnar interactions. The nature and mechanism of this exotic phase transition needs to be investigated more, particularly on the detailed crystal structure in the low-temperature phase.

IV. CONCLUSIONS

An isomorphous series is presented for mixed-stack CT complexes composed of BEDT-TTF-based electron donors and electron acceptors of halogen-substituted TCNQ's. It is found from the structural and optical measurements that both (BEDT-TTF)(Me₂TCNQ) and (BEDT-TTF)(CIME TCNQ) are neutral, while (BEDO-TTF)(Cl₂TCNQ) is ionic. In the

obtained complexes, the *side-by-side* intercolumnar overlaps are comparable to the *face-to-face* overlaps between the donor and acceptor molecules along the stacks, which is enough to suppress the spin-Peierls instabilities. Anomalous magnetic features were observed in the ionic compound of (BEDO-TTF)(Cl₂TCNQ), induced by the existing $S=1/2$ radical spins of the donor and acceptor molecules. Both the intercolumnar interactions and the complete ionicity ($\rho \sim 1$) characterize the various unconventional properties of (BEDO-TTF)(Cl₂TCNQ).

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