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Magnetic and Spectroscopic Studies of New Electrically Conducting Copper Complexes: 7,7,8,8-Tetracyanoquinodimethanides of Copper Chelates with Di-2-pyridylamine

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The electrically conducting Cu–TCNQ complexes Cu(dpa)$_2$(TCNQ)$_2$, Cu(dpa)$_2$(TCNQ)$_2$·H$_2$O, and Cu(dpa)(TCNQ)$_2$ (dpa = di-2-pyridylamine; TCNQ = 7,7,8,8-tetracyanoquinodimethan) have been obtained by reactions of [Cu(dpa)$_n$]$^{2+}$ and TCNQ$^{-}\cdot$. The single crystals of Cu(dpa)$_2$(TCNQ)$_2$ exhibited high electrical conductivity (ca. 50 Ω^{-1} cm^{-1} at 300 K) that displayed metal-like temperature dependence. Other materials obtained as powders showed a semiconductive property (0.56–4.5 Ω^{-1} cm^{-1} at 295 K) with a small activation energy in a range of 0.02–0.05 eV. These compounds were characterized by magnetic susceptibility, electron spin resonance, infrared, and thermoelectric power experiments. The results indicated that the formula of each compound is given by Cu^{+}(dpa)$_n$[(TCNQ)$_2$]$^{-}$ and also that one-dimensional lattices consisting of TCNQ$^{0.5-}$ yield the high electric conduction in every compound. The copper(II) chelates act as an appropriate oxidant against TCNQ$^{-}\cdot$ to form the highly conducting materials.

Introduction

Extensive efforts have been paid to the search for new "molecular metals" (i.e., nonmetallic materials exhibiting high electrical conductivity).[1] As part of the efforts, we have reported that a series of copper complexes with 7,7,8,8-tetracyanoquinodimethan, CuL$_n$(TCNQ)$_2$ (L = ethylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, or their derivatives), exhibited high powder conductivity amounting to 0.007–1.9 Ω^{-1} cm^{-1} at 300 K.[2,3] One of the features of these conducting materials is that their electrical properties including conductivity and thermoelectric power can be varied over a wide range by changing the coordinated ligands.[2–4] This is closely associated with the fact that the redox potential of copper in chelates changes over a wide range depending on the kind of coordinated ligands.[2–5] These studies suggest that use of copper chelates with appropriate ligands may afford a new way to design a wide variety of conducting TCNQ salts.

Recently, we have briefly reported that the single crystals of Cu(dpa)$_2$(TCNQ)$_2$ (dpa = di-2-pyridylamine) have high electrical conductivity (ca. 50 Ω^{-1} cm^{-1} at 300 K) that shows metal-like temperature dependence.[6] Melby et al.[7] reported, in their earliest work on TCNQ complexes, that Cu(dpa)(TCNQ)$_2$ showed high powder conductivity. The Cu(dpa)$_2$(TCNQ)$_2$ crystal conductivity, however, presented a new example of a metal-like TCNQ salt incorporating metal chelates as donors. The structural and electronic properties of the complex attract interest because they are thought to be important determinants of electron-transport properties. Single crystals suitable for X-ray crystal analysis have not been obtained. Magnetic and spectroscopic studies, however, can provide important information about molecular arrangements and electronic states of charge-transfer complexes. This paper reports the results of magnetic and spectroscopic studies including magnetic susceptibility, electron spin resonance (ESR), and infrared (IR) experiments carried out on the Cu(dpa)$_n$(TCNQ)$_2$ complexes together with their precise electrical data.

Experimental Section

Preparation of Cu(dpa)$_2$(TCNQ)$_2$. Cu(dpa)$_2$(NO$_3$)$_2$·2H$_2$O (19.9 mg) dissolved in an acetonitrile (1.5 mL)–methanol (15 mL) mixture was added to an acetonitrile (3 mL)–methanol (1 mL) solution dissolving LiTCNQ (13.9 mg) and TCNQ (7.6 mg) under a nitrogen atmosphere. The fine black needles that separated immediately were collected by filtration, washed with an acetonitrile–methanol (1:1) mixture, and dried under vacuum at room temperature. Anal. Calcd for C$_{44}$H$_{26}$N$_{14}$Cu: C, 64.9; H, 3.2; N, 24.1. Found: C, 65.1; H, 2.8; N, 24.5.

The single crystals were grown by a diffusion method as previously reported.[6]

Preparation of Cu(dpa)$_2$(TCNQ)$_2$·H$_2$O. A deaerated aqueous solution of Cu(dpa)$_2$(NO$_3$)$_2$·2H$_2$O (23.3 mg in 20 mL) was added to a deaerated aqueous solution of LiTCNQ (15.6 mg in 7 mL). A black precipitate formed immediately and was collected by filtration, washed with water, and dried under vacuum at room temperature. Anal. Calcd for C$_{44}$H$_{28}$N$_{14}$OCu: C, 63.5; H, 3.4; N, 23.6; H$_2$O, 2.2. Found: C, 63.1; H, 2.9; N, 23.2; H$_2$O, 1.9.[8]

Preparation of Cu(dpa)(TCNQ)$_2$. This material was prepared by a method reported already:[7] a metathesis of LiTCNQ with a CuCl$_2$·2H$_2$O–dpa (1:1) mixture in deaerated water.

Confirmation of Compound Formulas. In addition to elemental analyses, the compound formulas were confirmed by observing electronic spectra of acetonitrile solutions of the compounds by the use of a Varian DMS-80 UV-VL spectrophotometer. The intensity ratio of the 394- and 842-nm bands affords the TCNQ^{0}:TCNQ$^{-}\cdot$ ratio in solutions.[7,9] The ratio was determined to be unity for every compound investigated. As mentioned below, ESR experiments showed that the copper atoms of each compound are essentially in the Cu$^{\text{I}}$ state. Because each copper chelate has a +1 charge, the ratio TCNQ^{0}:TCNQ$^{-}\cdot$ = 1 leads to the compound formula Cu(dpa)$_n$(TCNQ)$_2$, in line with the results of elemental analyses.

IR Spectra. The IR spectra were recorded on Nujol and hexachlorobutadiene mulls of the compounds with a Perkin-Elmer 1420 spectrophotometer. Some vibrational modes of TCNQ shift largely depending on the charge occupation of TCNQ: TCNQ^{0} and TCNQ$^{-}\cdot$ exhibit the B$_u$-50 mode (CH bend) at 863 and 828 cm^{-1}, respectively.[4,10] In the spectrum of each material, the CH bend was observed at 840 ± 2 cm^{-1} (see Results) and neither the 863- nor the 828-cm^{-1} band was detected. This shows that the materials were not contaminated by TCNQ^{0} or TCNQ$^{-}\cdot$.

Electrical Properties. The electrical conductivity of powder samples was determined on the compressed pellets by van der Pauw's four-probe method.[11] The standard four-probe method was employed for determining the conductivity of single crystals. The Cu(dpa)$_2$(TCNQ)$_2$ crystals obtained had typical dimensions of 2 × 0.04 × 0.02 mm so that the conductivity was determined only along the needle axis. A sample crystal was mounted on Pt wires of 0.025-mm diameter with Aquadag. The mounted crystals were highly susceptible to thermal shock; the temperature dependence was difficult to study below ca. 200 K. The absolute value of the crystal conductivity involves a large error arising from difficulty in accurate determination of the crystal dimensions.

The thermoelectric power of the pellets was determined against copper metal at room temperature. The single crystals were too thin for this experiment.

Magnetic Susceptibilities.[12] The magnetic susceptibility was determined by means of a Faraday balance[13] at 0.5 T. Sodium chloride (−0.52 × 10^{-6} emu g^{-1}) was employed as a calibrant[13] because the magnetic susceptibilities of the compounds were very small. The molar susceptibility was corrected for diamagnetic contributions (10^{-6} emu mol^{-1}) from TCNQ (−121),[14] dpa (−97), and H$_2$O (−13).[15] The value of dpa was

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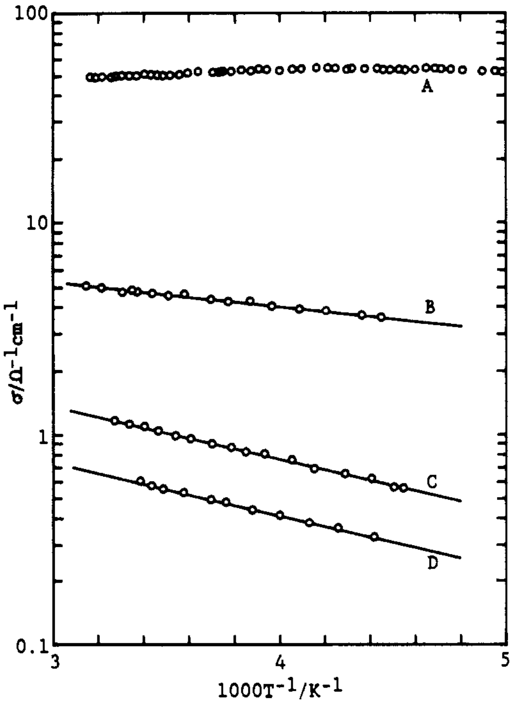

Figure 1. Electrical conductivity plotted against reciprocal temperature: A, $Cu(dpa)_2(TCNQ)_2$ single crystals; B, $Cu(dpa)_2(TCNQ)_2$ powders; C, $Cu(dpa)_2(TCNQ)_2{\cdot}H_2O$ powders; D, $Cu(dpa)(TCNQ)_2$ powders.

Table I. Electrical Data[a] for $Cu(dpa)_n(TCNQ)_2$: Electrical Conductivity σ/Ω^{-1} cm^{-1} at 295 K, Parameters $\sigma_\infty/\Omega^{-1}$ cm^{-1} and E/eV in $\sigma = \sigma_\infty \exp(-E/kT)$, and the Seebeck Coefficient $S/\mu V\ K^{-1}$

	σ	σ_∞	E	S
$Cu(dpa)_2(TCNQ)_2$				
powders	4.5	11	0.022	-80
single crystals	50	*b*	*b*	*c*
$Cu(dpa)_2(TCNQ)_2{\cdot}H_2O$	1.1	7.7	0.050	-75
$Cu(dpa)(TCNQ)_2$	0.56	4.1	0.050	-70

[a] The measurements were made on compressed pellets except as noted. [b] Metal-like temperature dependence. [c] Not determined.

evaluated on the basis of the Pascal constants.[15]

ESR Spectra. The ESR spectrum was recorded by the use of a Varian E-3 spectrometer. Diphenylpicrylhydrazyl (DPPH) was employed as a calibrant for determining *g* values.

Results

Electrical Conductivities. Figure 1 shows typical conductivity data observed for $Cu(dpa)_2(TCNQ)_2$ crystals along the needle axis. The observed temperature dependence varied slightly from sample to sample. All crystal samples subjected to the measurement, however, exhibited metal-like conductivity that increased with decreasing temperature until a broad maximum was reached. With further decrease of temperature, the conductivity decreased without showing a phase transition. This behavior resembles that of $(quinolinium)(TCNQ)_2$, one of the earliest known molecular metals.[16]

As shown in Figure 1, the dpa complexes obtained as powders exhibited thermally activated conductivity that is characteristic of semiconductors:

$$\sigma = \sigma_\infty e^{-E/kT} \tag{1}$$

where σ_∞ is conductivity at infinite temperature and E is the activation energy for electric conduction. The evaluated values of the parameters are collected in Table I, together with the conductivities at room temperature. The temperature dependence of the powder conductivity of molecular metals is governed by contact resistance between powder particles rather than by inherent electric conduction within particles. Because of the former extrinsic effect, powder materials usually show semiconducting properties (eq 1), even if the corresponding single crystals exhibit metallic conductivity: the powders of $(quinolinium)(TCNQ)_2$, for example, show a semiconductive property with an activation energy of 0.03 eV,[17] in spite of the fact that the crystal conductivity is metallic.[16] The electrical resistivity (40 Ω cm) reported by Melby et al.[7] for $Cu(dpa)(TCNQ)_2$ is larger than the value determined in our present study; the absolute value of powder conductivity is varied very often depending on the measurement method and/or the sample-preparation process. The activation energy reported by them,[7] however, agrees with our data. The activation energy determined for each powder material (Table I) is of order of magnitude predicted for the contact resistance between powder particles; the intrinsic conductivity of each material may be metallic.

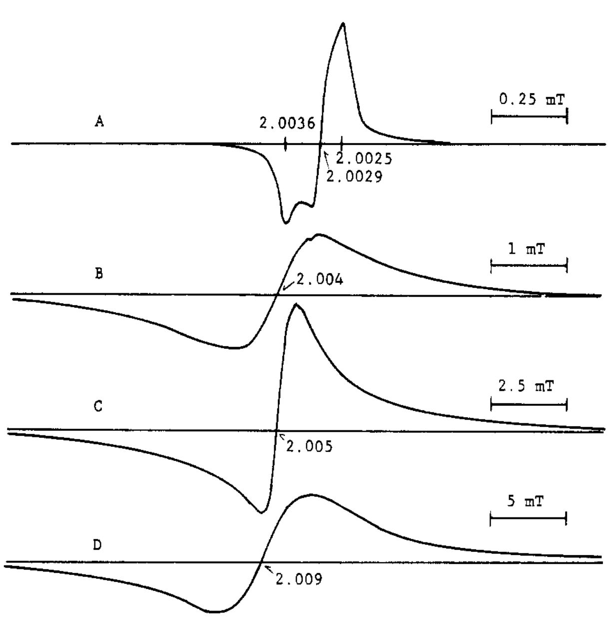

Figure 2. ESR spectra of $Cu(dpa)_2(TCNQ)_2$ pulverized crystals (A), $Cu(dpa)_2(TCNQ)_2$ powders (B), $Cu(dpa)_2(TCNQ)_2{\cdot}H_2O$ (C), and $Cu(dpa)(TCNQ)_2$ (D).

ESR Spectra. The single crystals of $Cu(dpa)_2(TCNQ)_2$ showed an angle-dependent ESR spectrum. Because no crystal data have been obtained, the single-crystal ESR experiment was carried out tentatively as follows. First, a single crystal was mounted on a uniaxial goniometer so that the needle axis of the crystal was perpendicular to the goniometer axis. Composite spectra were observed depending on crystal orientation. When the needle axis was parallel to the external magnetic field, a simple absorption derivative curve was displayed with the smallest *g* value. Accordingly, one of the principal axes of the crystal **g** tensor was assumed to coincide with the needle axis: $g_\parallel = 2.0027$. Then, the crystal was rotated about its needle axis to which the external magnetic field was applied perpendicularly. The observed spectrum was able to be resolved into two components with equal intensity; the separation between them was angle-dependent. The *g* values corresponding to the largest separation of the two components were assumed as the principal *g* components perpendicular to the needle axis: $g_\perp^{(1)} = 2.0030$ and $g_\perp^{(2)} = 2.0035$. The pulverized crystals exhibited a very sharp ESR signal with *g* anisotropy (Figure 2). This powder spectrum affords the principal components of the molecular **g** tensor: $g_1 = 2.0025$, $g_2 = 2.0029$, and $g_3 = 2.0036$. The averaged *g* value of 2.0030 agrees with that of LiTCNQ. The ESR signal of this compound is ascribable to $TCNQ^{-}\cdot$ ions. In a π-radical having an unpaired electron in its

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Table II. Magnetic and ESR Data for $Cu(dpa)_n(TCNQ)_2$: Magnetic Susceptibility χ/emu mol^{-1} per Compound Formula at 297 K, Corresponding Magnetic Moment μ/μ_B, Parameters in $\chi = \alpha + \gamma/T$, ESR g Value, Local Cu Susceptibility χ_{Cu}/emu mol^{-1} at Room Temperature, and Cu Oxidation Number N_{Cu}

	$\chi/10^{-4}$	μ	$\alpha/10^{-4}$	γ	g^a	$\chi_{Cu}/10^{-4}$	N_{Cu}
$Cu(dpa)_2(TCNQ)_2$							
powders	7.1	1.30	*b*	*b*	2.004	0	1
crystals	8	1.4	*b*	*b*	2.0025 2.0029 2.0036	0	1
$Cu(dpa)_2(TCNQ)_2 \cdot H_2O$	10.2	1.56	8.1	0.062	2.005	0.2	1.02
$Cu(dpa)(TCNQ)_2$	6.0	1.20	5.6	0.0125	2.009	0.4	1.03

[a] Pulverized crystals of $Cu(dpa)_2(TCNQ)_2$ showed an ESR signal with g anisotropy. For other powder materials, a simple ESR signal was observed. [b] Very weak temperature dependence.

p orbital, the g component parallel to the axial symmetry axis of the orbital is unchanged from the free-electron value, 2.0023;[18] in an aromatic radical, the axis of the principal g component closest to 2.0023 lies perpendicular to the molecular plane. The axis of the smallest g component $g_1 = 2.0025$ of $Cu(dpa)_2(TCNQ)_2$ can be assumed to lie perpendicular to the molecular plane of TCNQ. This value is very close to the crystal g value $g_\parallel = 2.0027$ observed along the crystal needle axis. This suggests that every TCNQ radical is arranged in such a way that its molecular plane is almost perpendicular to the crystal needle axis. The TCNQ molecules are probably stacked face-to-face along the axis. This type of molecular arrangement has been commonly found in highly conductive TCNQ salts.[1] The stack direction coincides with that of the highest electric conduction in crystals. $Cu(dpa)_2(TCNQ)_2$ obtained as powders showed a single ESR signal with $g = 2.004$ (Figure 2). This value practically agrees with the g value 2.003 of LiTCNQ: the ESR signal arises from $TCNQ^{-}\cdot$ ions. The ESR spectra of both $Cu(dpa)_2(TCNQ)_2$ crystals and powders showed no signal attributable to Cu^{2+} ions. The copper atoms of the materials are in the diamagnetic Cu^{I} state.

$Cu(dpa)(TCNQ)_2$ showed a single asymmetric ESR signal with $g = 2.009$ (Figure 2). This value is significantly larger than the value 2.003 of $TCNQ^{-}\cdot$ and is much smaller than the value 2.1 observed normally for Cu^{2+} ions. In a spin system involving two different kinds of paramagnetic species coupled strongly with each other, its ESR signal is centered at a position corresponding to an average of the individual g values.[19,20] Because each $Cu(dpa)(TCNQ)_2$ unit involves a copper atom and two TCNQ molecules, the averaged g value is given by

$$g = (\chi_{Cu} g_{Cu} + 2\chi_{TCNQ} g_{TCNQ})/\chi_{total} \tag{2}$$

$$\chi_{total} = \chi_{Cu} + 2\chi_{TCNQ} \tag{3}$$

In these equations, g_{Cu} and g_{TCNQ} are the g values of copper and TCNQ, respectively, χ_{Cu} is local magnetic susceptibility contributed from copper, χ_{TCNQ} is that from TCNQ, and χ_{total} is total magnetic susceptibility, which can be equated with static magnetic susceptibility that is determinable with a magnetic balance. The magnetic susceptibility of this compound was determined as 6.0×10^{-4} emu mol^{-1} per compound formula at 297 K (Table II). From eq 2 and 3, χ_{Cu} was evaluated as ca. 0.4×10^{-4} emu mol^{-1} by assuming that $g_{Cu} = 2.1$ and $g_{TCNQ} = 2.003$. A free-electron system in which an isolated unpaired electron exists on each site has a magnetic susceptibility χ_s (in emu mol^{-1}) given by the Curie law as a function of temperature T:

$$\chi_s = 0.375/T \tag{4}$$

The ratio of χ_{Cu} to χ_s yields an unpaired electron density residing on a copper site. The density was evaluated as 0.03 for $Cu(dpa)(TCNQ)_2$. The unpaired electron density plus 1 gives the average oxidation number 1.03 of copper. This leads to the following conclusions. First, the copper(II) chelates employed as starting materials are reduced to the Cu^{I} state in the course of the complex formation. Second, in the resulting complex, a partial electron transfer takes place between copper and TCNQ, accompanying probably the so-called solid-state equilibrium

$$Cu^{+}(dpa)[(TCNQ)_2]^{-}\cdot \rightleftharpoons Cu^{2+}(dpa)(TCNQ^{-}\cdot)_2 \tag{5}$$

The right-hand side contributes 3% to the equilibrium, resulting in the mixed-valence (or intermediate oxidation) state of copper. The ESR spectrum observed for this compound is slightly asymmetric (Figure 2). The g anisotropy of usual copper(II) complexes is very large compared with that of organic radicals. When the g anisotropy of copper complexes is incompletely smeared out by a magnetic interaction, a single asymmetric ESR spectrum is observed. The asymmetric signal of $Cu(dpa)(TCNQ)_2$ also is suggestive of the existence of the unpaired electron density on copper.[21]

The g value 2.005 of $Cu(dpa)_2(TCNQ)_2 \cdot H_2O$ is nearly equal to that of $TCNQ^{-}\cdot$: the ESR spectrum arises essentially from $TCNQ^{-}\cdot$. The observed signal, however, is asymmetric (Figure 2): unpaired electrons may reside partly on copper. By the same procedure as employed for $Cu(dpa)(TCNQ)_2$, unpaired electron density on copper was tentatively estimated to be 0.02 from the observed g value. Probably, a solid-state equilibrium similar to eq 5 takes place also in this compound so that each copper has an intermediate oxidation number of ca. 1.02 on average.

The ESR signal observed for $Cu(dpa)_2(TCNQ)_2$ crystals was markedly narrow: the maximum slope width was as small as 0.06 mT when the needle axis was parallel to the external field. The narrow ESR signal is characteristic of highly conducting materials that have a very high spin-exchange frequency (or large exchange interaction energy). The ESR spectra of the powder materials were broad compared with the spectrum of $Cu(dpa)_2(TCNQ)_2$ crystals: the maximum slope width was observed as 1.1 mT for $Cu(dpa)_2(TCNQ)_2$ powders, 1.2 mT for $Cu(dpa)_2(TCNQ)_2 \cdot H_2O$, and 5.6 mT for $Cu(dpa)(TCNQ)_2$. The spin exchange is much slower in the powder materials than in $Cu(dpa)_2(TCNQ)_2$ crystals.

Magnetic Susceptibilities. Table II collects the magnetic susceptibilities of the compounds per compound formula at room temperature.

The magnetic susceptibility of $Cu(dpa)_2(TCNQ)_2$ powders decreased gradually with decreasing temperature: 7.1×10^{-4} emu mol^{-1} at 297 K and 6.2×10^{-4} emu mol^{-1} at 126 K. For pulverized $Cu(dpa)_2(TCNQ)_2$ crystals, the susceptibility was difficult to determine accurately because of the small sample amount. Within the experimental error, however, it was temperature-independent. These paramagnetisms are ascribed to unpaired electrons of $[(TCNQ)_2]^{-}$ units because the ESR experiments show that the copper atoms are in the Cu^{I} state. The weak temperature dependence cannot be interpreted in terms of a simple singlet–triplet excitation model. The effective magnetic moments per compound formula are much smaller than the value 1.73 μ_B predicted for an isolated spin. These indicate that a strong magnetic interaction is operative between $[(TCNQ)_2]^{-}$ units. The weak temperature

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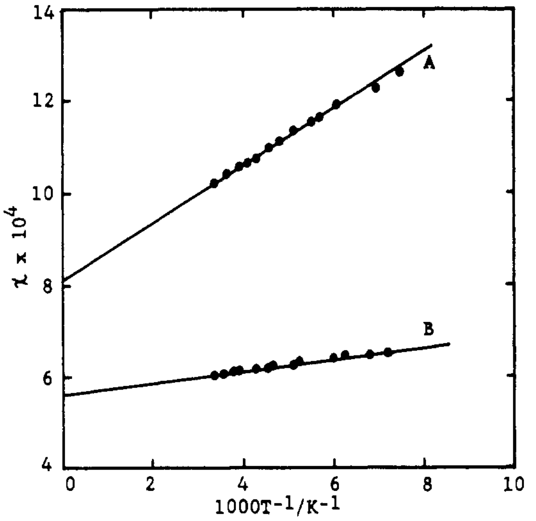

Figure 3. Magnetic susceptibility χ (in emu mol^{-1}) plotted against reciprocal temperature: A, $Cu(dpa)_2(TCNQ)_2 \cdot H_2O$; B, $Cu(dpa)(TCNQ)_2$.

dependence of susceptibility is characteristic of highly conducting one-dimensional solids: it has been observed for (quinolinium)$(TCNQ)_2$,[22] Ni(phthalocyanine)I,[23] etc. The magnetic susceptibilities of $Cu(dpa)_2(TCNQ)_2$ materials are suggestive of the existence of TCNQ columns in which unpaired electrons are extensively delocalized. This is consistent with the ESR results.

The magnetic susceptibility of $Cu(dpa)(TCNQ)_2$ increases with decreasing temperature, but it does not obey the Curie–Weiss law. Figure 3, in which the magnetic susceptibility is plotted against reciprocal temperature, shows that the susceptibility can be reproduced well with the equation

$$\chi = \alpha + \gamma/T \qquad (6)$$

This type of temperature dependence has been observed for some conducting TCNQ salts of copper chelates:[2,20] α is ascribed to the temperature-independent paramagnetism of delocalized conduction electrons, and γ/T is attributed mainly to localized unpaired electrons. The α and γ values evaluated for $Cu(dpa)(TCNQ)_2$ are shown in Table II. A spin system in which an unpaired electron resides isolatedly on each magnetic site shows the Curie-type paramagnetism that is given by eq 4. When the γ/T term originates from localized spins, the ratio of γ to 0.375 (the Curie constant in eq 4) gives an unpaired-electron density on each site. For $Cu(dpa)(TCNQ)_2$, the γ value affords the density 0.03, which agrees with the unpaired-electron density on copper evaluated from the ESR g value. This agreement provides evidence showing that each copper atom has the intermediate oxidation number 1.03, yielding the γ/T term. The temperature-independent paramagnetic term $\alpha = 5.6 \times 10^{-4}$ emu mol^{-1} of $Cu(dpa)(TCNQ)_2$ is much larger than the uncertainty (ca. 10%) presumable for the employed diamagnetic correction (3.39×10^{-4} emu mol^{-1}): the α term is not due to an overestimation of the diamagnetic correction, but it arises from the intrinsic nature of TCNQ electrons. The α value is nearly equal to the magnetic susceptibility 7×10^{-4} emu mol^{-1} of $Cu(dpa)_2(TCNQ)_2$ and also to 5×10^{-4} emu mol^{-1} of (quinolinium)$(TCNQ)_2$.[22] The magnetic property of the TCNQ array is essentially the same among these compounds. The ESR result showed that a spin-exchange interaction operates between copper and TCNQ with an energy larger than that corresponding to the g-value difference of the two paramagnetic species. On the other hand, the local copper and TCNQ susceptibilities, which are given by the γ and α terms, respectively, were determined separately: the energy of the magnetic interaction between copper and TCNQ is negligibly small compared with the thermal energy in the temperature range of the present magnetic susceptibility study.

Figure 3 shows that the magnetic susceptibility of $Cu(dpa)_2(TCNQ)_2 \cdot H_2O$ also can be reproduced with eq 6. The evaluated α value 8.1×10^{-4} emu mol^{-1} is much larger than the uncertainty presumable for the employed diamagnetic correction (4.49×10^{-4} emu mol^{-1}), and it is nearly equal to the magnetic susceptibility of $Cu(dpa)_2(TCNQ)_2$. The α term is intrinsic to the conducting TCNQ lattices. The ratio γ:0.375 = 0.17 of $Cu(dpa)_2(TCNQ)_2 \cdot H_2O$ disagrees with the unpaired-electron density 0.02 on copper evaluated from the g value. The ESR spectrum showed no detectable impurity signal. Accordingly, the disagreement is not due to paramagnetic impurities, although the impurity effect is not entirely avoidable in charge-transfer complexes.[14] Two effects are conceivable for the large γ value. First, unpaired electrons localized on crystal defects such as chain ends yield the Curie-type paramagnetism. Second, the susceptibility of conduction electrons increases with decreasing temperature when the conduction band is so narrow that $kT << E_F$ (E_F = Fermi energy) does not hold.[20,24] The first effect has been observed for many one-dimensional solids.[14,22,25] The second type of paramagnetic behavior has been found for Cu(2,2′-bipyridine)$(TCNQ)_2$ and Cu(ethylenediamine)$(TCNQ)_2$.[20]

IR Spectra. All materials exhibited essentially the same IR spectral patterns. A broad intense band appears at ca. 2900 cm^{-1} and extends down to an edge at ca. 1000 cm^{-1}. On the envelope, some vibrational bands are superimposed: the $C{\equiv}N$ stretch appears at 2240 cm^{-1}. Below the band edge, a single vibrational band assignable to the B_u-50 mode[10] appears at 840 ± 2 cm^{-1} in every spectrum.

Complete assignments have been carried out on the vibrational bands of both neutral $TCNQ^0$ molecules and $TCNQ^{-}\cdot$ ions.[10] Some vibrational modes show a large frequency shift depending on the charge occupation of TCNQ.[10] The IR bands can be employed for determining the formal charge of TCNQ. For example, $Cu(TCNQ)_2$, which has the formula $Cu^+(TCNQ^-\cdot)(TCNQ^0)$,[26,27] exhibits two B_u-50 IR bands at 827 and 864 cm^{-1}:[4] the former is attributed to $TCNQ^-\cdot$ and the latter to $TCNQ^0$. The A_g-4 mode appearing in Raman spectra has been shown to shift linearly with the charge occupation of TCNQ.[28] On the basis of this relation, the presence of a fractional charge on TCNQ has been demonstrated for some charge-transfer TCNQ complexes.[28] If the linear relation is assumed to hold for the B_u-50 mode, the charge occupation of TCNQ can be evaluated as 0.6 for every compound by using 827 and 864 cm^{-1} as the extreme values of $TCNQ^-\cdot$ and $TCNQ^0$, respectively. The obtained charge density is not so accurate because of limitations of the applicability. This tentative evaluation, however, evidently shows that each compound involves a single species of TCNQ carrying a fractional charge. This indicates that each compound has essentially the formula $Cu^+(dpa)_n[(TCNQ)_2]^-$ in which two TCNQ constituents share an electronic charge equivalently, in accordance with the magnetic study result showing that the copper atoms of each compound are in the +1 oxidation state.

Thermoelectric Powers. The Seebeck coefficient determined on the compressed pellets of each compound fell in a range of −70 to −80 $\mu V\ K^{-1}$. The thermoelectric power generated in $R^+[(TCNQ)_n]^-$ type complexes can be interpreted well by the so-called on-site interaction model,[29,30] which affords the Seebeck coefficient S given by

$$S = -(k/|e|) \ln [2(1 - \rho)/\rho] \qquad (7)$$

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Here, apart from the universal constants, ρ is the ratio of particle to TCNQ sites. The negative Seebeck coefficients observed for the dpa complexes indicate that the current carriers are electrons in the complexes. On the basis of eq 7, ρ is evaluated as 0.44–0.47 from the observed Seebeck coefficients, supporting the formula $Cu^+(dpa)_n(TCNQ^{0.5-})_2$.

Discussion

The above mentioned data concerning molecular arrangement in the complexes are summarized as follows: (1) the IR spectra showed the presence of single TCNQ species in every compound, (2) the magnetic susceptibility ascribed to TCNQ of each compound exhibited weak temperature dependence, which is characteristic of conducting one-dimensional solids, and (3) the ESR spectrum of $Cu(dpa)_2(TCNQ)_2$ crystals indicated that the TCNQ molecules are stacked along the needle axis. These suggest that a TCNQ column structure is formed in every $Cu(dpa)_n(TCNQ)_2$ complex as commonly found in highly conducting TCNQ salts.[1]

The results of thermoelectric power and IR experiments evidently showed that each TCNQ molecule carries a fractional charge on the average. This along with the ESR study result proposes the formula $Cu^+(dpa)_n(TCNQ^{0.5-})_2$. A column consisting of $TCNQ^{0.5-}$ may form a half-filled band, resulting in metal-like electric conduction. This has been demonstrated by the metal-like conductivity of $Cu(dpa)_2(TCNQ)_2$ crystals. Probably, the powder materials also have intrinsically a metallic property within powder particles (or small domains).

A broad intense band has been observed for many TCNQ salts in the near-IR region.[9,31] One of well-characterized examples is given by (tetraethylammonium)$(TCNQ)_2$,[32] which shows a broad absorption band at ca. 3000 cm^{-1} with a sharp edge at ca. 1600 cm^{-1}. This absorption band has been interpreted in terms of an electronic transition between TCNQ bands.[32] The broad intense band observed with an absorption maximum at 2900 cm^{-1} for each $Cu(dpa)_n(TCNQ)_2$ compound also can be ascribed to an electronic transition. Every spectrum displays the same absorption pattern. This may suggest that essentially the same TCNQ band structure is formed in all complexes investigated.

The copper atoms of each $Cu(dpa)_n(TCNQ)_2$ compound are practically in the +1 oxidation state. In the course of the complex formation, $Cu^{2+}(dpa)_n$ chelates oxidize $TCNQ^{-}\cdot$ partially to yield $Cu^+(dpa)_n(TCNQ^{0.5-})_2$. The resulting fractional charge on TCNQ leads to the metal-like conductivity in the TCNQ lattices. The copper chelates are indispensable for forming current carriers on the TCNQ arrays. An intermediate oxidation state (or mixed-valence state) of constituent molecules is one of important features found commonly in molecular metals.[1] The formation of chemical species with a mixed-valence state may be accomplished by selecting an appropriate oxidant or reductant.[33] Copper(II) chelates can function as excellent oxidizing agents against $TCNQ^{-}\cdot$ so that they can afford highly conducting TCNQ salts.

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Registry No. $Cu(dpa)_2(TCNQ)_2$, 93855-33-5; $Cu(dpa)_2(TCNQ)_2 \cdot H_2O$, 98194-40-2; $Cu(dpa)(TCNQ)_2$, 98194-42-4; $Cu(dpa)_2(NO_3)_2$, 14128-83-7.

Supplementary Material Available: Figures of χ vs. T plots for $Cu(dpa)_n(TCNQ)_2$ and the IR spectrum of $Cu(dpa)_2(TCNQ)_2$ (2 pages). Ordering information is given on any current masthead page.

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Tris(*o*-phenylenedioxy)cyclotriphosphazene: The Clathration-Induced Monoclinic to Hexagonal Solid-State Transition

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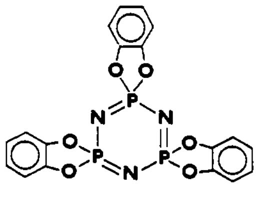
Tris(*o*-phenylenedioxy)cyclotriphosphazene (I) is known to clathrate a variety of small molecules. The clathration process coincides with a solid-state transformation of the host from a monoclinic, guest-free form to a hexagonal, guest-containing modification, a process that involves a 23% volume expansion. The transition occurs in response to improved opportunities for van der Waals attraction as guest molecules enter the lattice. Scanning electron microscopy revealed that considerable crystal disruption occurs during the transition. The resultant microcrystallites were fairly uniform in size and morphology. Crystals of I are monoclinic, space group $P2_1/n$, with eight formula units in a unit cell of dimensions a = 25.086 (5) Å, b = 5.911 (2) Å, c = 25.913 (7) Å, and β = 95.97 (2)°. The water adduct of I (II), crystallizes in the hexagonal space group $P6_3/m$ with two molecules in a unit cell of dimensions a = 11.606 (4) and c = 10.087 (3) Å. Both structures were solved by direct methods and refined by full-matrix least-squares calculations to R = 0.075 and R_w = 0.082 for 2341 reflections for I and to R = 0.050 and R_w = 0.056 for 287 reflections for II.

Introduction

Tris(*o*-phenylenedioxy)cyclotriphosphazene (I) is the simplest member of a class of spirocyclic phosphazene molecules that form tunnel inclusion adducts.[1-9] The clathration process can be used to separate different guest molecules from mixtures,[1,3] and the clathrates themselves provide a means for the storage of unstable



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