Tetracyanoquinodimethan Salts of a Copper Chelate with Tetrabenzo[b, f, j, n][1,5,9,13]tetraazacyclohexadecine: Electrical Properties and Mixed-Valence States

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Metatheses between lithium tetracyanoquinodimethanide, $Li(TCNQ^{\bullet-})$, and the copper chelate with tetrabenzo[b, j, n]-[1,5,9,13]tetraazacyclohexadecine (taab) yielded semiconductive complexes $Cu(taab)(TCNQ)_n$ (n = 1.5 or 2): the conductivities were 0.015 and 0.04 S cm⁻¹ for Cu(taab)(TCNQ)₂ and Cu(taab)(TCNQ)_{1.5}, respectively, at 300 K, and the activation energies were 0.086 eV for the former and 0.058 eV for the latter. These complexes were characterized with the aid of electron spin resonance, infrared, and X-ray photoelectron spectroscopies and magnetic susceptibility measurements. The compounds can be formulated as $[Cu^{1}(taab)]^{+}[(TCNQ)_{n}]^{\bullet-}$; a partial electron transfer occurs from $[Cu^{1}(taab)]^{+}$ to $[(TCNQ)_{n}]^{\bullet-}$ and results in a nonintegral oxidation number for copper.

Introduction

A series of electroconductive copper-TCNQ complexes, $CuL_n(TCNQ)_2$ (TCNQ is 7,7,8,8-tetracyanoquinodimethan, L is ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline, or di-2-pyridylamine), has been prepared by metatheses between Li-(TCNQ^{•-}) and [$Cu^{II}L_n$]X₂.¹⁻⁴ The electrical properties of these complexes vary over a wide range with the nature of the coordinated ligands. With respect to the oxidation state of copper, the compounds are classified into two groups:^{2,4,5} (1) the copper atoms of the complexes with the aromatic heterocycles are practically in the Cu^{II} state and (2) the copper atoms of the ethylenediamine complex are in the Cu^{II} state. The formation of the former complexes accompanies the following redox reaction:

$$[\operatorname{Cu}^{\mathrm{II}} \mathrm{L}_n]^{2+} + 2(\operatorname{TCNQ}^{\bullet-}) \rightarrow [\operatorname{Cu}^{\mathrm{I}} \mathrm{L}_n]^+[(\operatorname{TCNQ})_2]^{\bullet-} \quad (1)$$

The difference in the oxidation state of copper arises obviously from the difference in the stabilization of the Cu¹ state upon the coordination of ligands. This difference results in the diversity of electrical properties of the copper complexes: for example, Cu¹(dpa)₂(TCNQ)₂ (dpa is di-2-pyridylamine) exhibits metal-like conductivity (50 S cm⁻¹ along the crystal needle axis at 300 K),⁴ whereas Cu^{II}(en)₂(TCNQ)₂ (en is ethylenediamine) is a p-type semiconductor with powder conductivity equal to 7×10^{-4} S cm⁻¹ at 300 K.¹

A tetraaza[16]annulene ligand, tetrabenzo[b, j, n][1,5,9,13]tetraazacyclohexadecine (taab) forms a copper(II) chelate, $[Cu(taab)]^{2+}$

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which has a square planar coordination.⁶ This chelate can be readily reduced to $[Cu(taab)]^{+,7}$ Since the d¹⁰ electron configuration of copper is not favored by the square planar coordination geometry, the formula $[Cu^{III}(taab^{2-})]^{+}$ was proposed.⁷ This formula, however, has been ruled out by a recent X-ray photoelectron spectroscopic (XPS) study:⁸ the Cu 2p-core electron spectra observed are characteristic of authentic Cu^I species. This peculiarity of the taab complexes has directed our interest to the reaction of $[Cu(taab)]^{2+}$ with TCNQ⁺⁻ and also to the physical properties and electronic structures of the resulting compounds. In the present study, we have obtained Cu(taab)(TCNQ)₂ (1) and $[Cu(taab)]_2(TCNQ)_3$ (2) that show high electrical conduc-

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tivities; these compounds have been characterized with the aid of electron spin resonance (ESR), infrared (IR) spectroscopy, XPS, and magnetic susceptibility measurements.

Experimental Section

Preparation of 1. When a deaerated aqueous solution of $Cu(taab)(NO_3)_2^9$ (0.021 mmol in 8.5 mL) was added to a deaerated aqueous solution of Li(TCNQ) (0.04 mmol in 3.5 mL) with stirring under a nitrogen atmosphere, a deep green precipitate was formed. After the resulting mixture was stirred for ca. 1 h, the precipitate was collected on a filter, washed with deaerated water, and dried under vacuum. Anal. Calcd for $C_{52}H_{28}N_{12}Cu$: C, 70.62; H, 3.19; N, 19.01; Cu, 7.19. Found: C, 69.90; H, 3.21; N, 18.41; Cu, 7.36.

Preparation of 2. When methanol was employed as a solvent instead of water, 2 was obtained as a deep green powder. The precipitate formed from the methanol solution was collected on a filter, washed with methanol, and dried under vacuum. Anal. Calcd for $C_{46}H_{26}N_{10}Cu$: C, 70.63; H, 3.35; N, 17.91; Cu, 8.13. Found: C, 70.15; H, 3.32; N, 17.21; Cu, 8.13.

Confirmation of Compound Formulas. The composition of the two compounds was confirmed with the aid of solution electronic spectra as follows. The charge residing on each Cu(taab) chelate of the Cu-TCNQ complexes was determined to be approximately equal to +1 by ESR and XPS experiments (see Results and Discussion):¹⁰ the formula is given as [Cu-(taab)]⁺[(TCNQ)_n]⁺⁻. In solution, each [(TCNQ)_n]⁺⁻ unit dissociates into TCNQ⁺⁻ and (n - 1) (TCNQ⁰). The ratio TCNQ⁰:TCNQ⁺⁻ in solution can be determined by measuring the intensity ratio of the 843- and 394-nm bands of the solution spectra.¹¹ The electronic spectra of the compounds were recorded for the acetonitrile solutions by the use of a Varian DMS-80 UV-VL spectrophotometer and reasonable TCNQ⁰:TCNQ⁺⁻ ratios were obtained: 0.8 for 1 and 0.4 for 2. These data support the compound formulas determined by elemental analyses.¹⁰ The IR spectra showed that the materials were not contaminated by TCNQ⁰ liberated in the solids (see Results and Discussion).

Physical and Spectroscopic Measurements. Electrical conductivities of the compressed pellets were determined by van der Pauw's four-probe method.¹² The thermoelectric power was measured against copper metal with platinum contacts.

The IR spectra were recorded on Nujol mulls with a Perkin Elmer 1420 spectrophotometer. The nature of the spectra observed was independent of the condition of the mulls.

The ESR spectra were recorded by the use of a Varian E-3 spectrometer. Diphenylpicrylhydrazyl (DPPH) was used as a calibrant for the determination of g values.

The XPS was obtained by the use of a Vacuum Generators ESCALAB MKII spectrometer (East Grinstead, U.K.) with Al K α X-rays (1486.6 eV). The sample powders were mixed with powdered graphite in a ratio of 15:1 and pressed onto indium foil. The binding energies of the photoelectrons were determined by assuming that the carbon 1s electrons had a binding energy of 284.6 eV. The data were recorded digitally and all peak scans were signal averaged until an acceptable signal-to-noise ratio was obtained. During the experiments, the pressure in the sample chamber did not exceed 5×10^{-10} Torr, and a significant outgassing of the sample did not occur. There was no indication of sample decomposition due to the X-ray irradiation.

The magnetic susceptibilities were determined with a Faraday balance.¹³ Sodium chloride $(-0.52 \times 10^{-6} \text{ emu g}^{-1})$ and copper(II) sulfate pentahydrate $(5.85 \times 10^{-6} \text{ emu g}^{-1} \text{ at } 300 \text{ K})$ were employed as calibrants.¹³ The molar susceptibilities were corrected



Figure 1. ESR spectra of $Cu(taab)(TCNQ)_2$ (A) and $Cu(taab)-(TCNQ)_{1.5}$ (B).

for diamagnetic contributions $(10^{-6} \text{ emu mol}^{-1})$ from taab (-218) and TCNQ (-121).¹⁴ The former value was calculated from Pascal's constants.¹⁵

Results and Discussion

Electrical Properties. The powder conductivities were 0.015 S cm⁻¹ for 1 and 0.04 S cm⁻¹ for 2 at 300 K. The variation of the conductivity σ with temperature T followed eq 2 throughout

$$\sigma = \sigma_{\infty} e^{-E/kT} \tag{2}$$

the temperature range investigated, 200-300 K. The activation energy E was calculated to be 0.086 eV for 1 and 0.058 eV for 2. The Seebeck coefficients of thermoelectric power were negative: $-65 \ \mu V \ K^{-1}$ for 1 and $-80 \ \mu V \ K^{-1}$ for 2. The compounds are n-type semiconductors.

ESR and IR Spectra. Figure 1 shows the ESR spectra observed for the complexes at room temperature: 1 exhibited an asymmetric signal centered at g = 2.012 with W_{msl} (maximum slope width) ~ 24 G, whereas 2 gave a sharp signal with g = 2.004 and W_{msl} ~ 2 G. The g value of 2 involved an uncertainity of ± 0.001 , because the signal width was almost the same as that of DPPH employed as a calibrant.

The observed g values were nearly equal to the value 2.003 for Li(TCNQ⁻⁻), and the spectrum patterns were different from that of Cu(taab)(NO₃)₂, which exhibited an ESR signal characteristic of Cu²⁺ ions in an axially symmetric field and had $g_{\parallel} = 2.18$ and $g_{\perp} = 2.03$. In the spectrum of each Cu–TCNQ complex, a signal attributable to Cu²⁺ ions was not detected. These results indicate that the ESR signals arise from TCNQ⁻⁻ ions rather than Cu²⁺ ions. Accordingly, the copper chelate is formulated as [Cu(taab)]⁺ that has no unpaired electron.

Both compounds showed practically the same IR spectra. A broad intense band extended from 4000 to 900 cm⁻¹. This is ascribable to an electronic absorption, which has been observed for some conducting TCNQ salts.^{5,16} On the absorption envelope, vibrational bands are superimposed. Three C=N stretching bands of TCNQ appeared at 2160, 2180, and 2210 cm⁻¹. Other TCNQ bands were difficult to distinguish from Cu(taab) bands. Below the edge of the electronic absorption band, two weak but unmistakable bands were observed at 825 and 838 cm⁻¹ in the CH bending region (Figure 2). A comparison of the spectrum with that of Cu(taab)(BF₄)₂ shows that the 825-cm⁻¹ band can be attributed to taab and hence the 838-cm⁻¹ band to TCNQ (Figure

⁽⁹⁾ This material was prepared by the method reported in ref 6 and was confirmed by its IR spectrum.

⁽¹⁰⁾ An accurate analysis of the ESR spectra showed that the copper atoms are in a mixed-valence state (see Results and Discussion): for example, each copper chelate in 1 carries ± 1.07 charge. The TCNQ⁰:TCNQ⁺⁻ ratio is calculated to be 0.87 for [Cu(taab)]^{1.07+}[(TCNQ)₂]^{1.07+-}.

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Figure 2. IR spectra of $Cu(taab)(TCNQ)_{1.5}$ (A), $Cu(taab)(BF_4)_2$ (B), and $Cu^{I}(TCNQ^{\bullet})(TCNQ^{0})$ (C).

2). This mode of TCNQ exhibits a large frequency shift upon ionization.^{5,17} For example, $Cu(TCNQ)_2$, which can be formulated as $Cu^{I}(TCNQ^{\bullet-})(TCNQ^{0})$, shows two CH bending frequencies at 827 and 864 cm⁻¹: the former is attributed to TCNQ⁺⁻ and the latter to TCNQ^{0,5} On the other hand, $[Cu(dpa)_2]^{+-}$ $[(TCNQ)_2]^{\bullet-}$, which involves TCNQ^{0,5+-}, shows a single CH bend at a wavenumber of 840 cm⁻¹ that is intermediate between 827 and 864 cm⁻¹.⁴ The TCNQ bands of both 1 and 2 appeared at 838 cm⁻¹, indicating a fractional charge occupation of TCNQ. No band was observed at 864 cm⁻¹ in the spectrum of either compound; the materials did not contain TCNQ⁰ as intrinsic constituents or as contaminants.

The above ESR and IR results lead to the formulation [Cu-(taab)]⁺[(TCNQ)_n]^{•-}, in which each TCNQ moiety carries an equal fractional charge. The complex formation accompanies the redox reaction of the same type as eq 1.

The g value of 1 is significantly larger than the value 2.003 for $Li(TCNQ^{\bullet-})$. This, together with the asymmetric line shape, requires that the unpaired electrons of TCNQ are coupled with copper atoms. A partial electron transfer occurs from $[Cu(taab)]^+$ to $[(TCNQ)_n]^{\bullet-}$ so that the complex is in a "solid-state equilibrium"

$$[Cu(taab)]^{+}[(TCNQ)_{2}]^{\bullet-} \rightleftharpoons [Cu(taab)]^{2+}(TCNQ^{\bullet-})_{2} (3)$$

When an unpaired electron distributes on two different kinds of magnetic sites, the g value is equated with an average of the respective g values in the strong coupling limit.^{18,19} For the compound formula of 1, an unpaired electron is coupled with one copper atom and two TCNQ moieties. Therefore, the g value is given by

$$g = (g_{Cu}\chi_{Cu} + 2g_{TCNQ}\chi_{TCNQ})/(\chi_{Cu} + 2\chi_{TCNQ})$$
(4)

where g_{Cu} and g_{TCNQ} are the g values of copper and TCNQ, respectively, χ_{Cu} is the local susceptibility of copper, and χ_{TCNQ} is that of TCNQ. The total susceptibility, $\chi_{Cu} + 2\chi_{TCNQ}$, can be equated with the static susceptibility that is determinable with a magnetic balance technique. The molar susceptibility determined for the compound formula was equal to 7.9×10^{-4} emu mol⁻¹ at 300 K. The g_{Cu} in eq 4 can be assumed to be equal to the averaged



Figure 3. XPS spectra of $Cu(taab)(TCNQ)_2$ (A) and $Cu(taab)(TCNQ)_{1.5}$ (B).

g value of Cu(taab)(NO₃)₂: $[(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{1/2} = 2.08$. By the use of this value and 2.003 for g_{TCNQ} , χ_{cu} can be evaluated to be 0.9×10^{-4} emu mol⁻¹. The spin system that has one unpaired electron on each magnetic site exhibits a magnetic susceptibility χ_s given by the Curie law

$$\chi_s = 0.375 / T$$
 (5)

The ratio $\chi_{Cu}:\chi_s$ gives the mean number of unpaired electrons residing on each copper site: each copper chelate carries a fractional unpaired electron of 0.07 on the average. The right-hand side of eq 3 contributes 7% to the equilibrium; the mean oxidation number of copper is 1.07.

The g value of 2 was practically the same as the value 2.003 for $Li(TCNQ^{-})$. The asymmetric line shape, however, suggests that the unpaired electrons of TCNQ are also coupled partially with copper in this compound. A g shift of 0.001 from 2.003 is accomplished by the delocalization of 0.005 spin to each copper site on the average. The contribution of the right-hand side in eq 3 is of this order of magnitude.

XPS. Figure 3 shows the copper 2p core electron spectra of the complexes. Main peaks arising from the $2p_{1/2}$ and $2p_{3/2}$ electrons were located at 952.0 \pm 0.2 and 932.1 \pm 0.2 eV, respectively, in each spectrum.

The $2p_{3/2}$ peak of 1 showed an unmistakable shoulder at an energy ca. 2.5 eV higher than that of the main peak. Gagné et al.8 carried out XPS studies on pairs of Cu¹ and Cu¹¹ complexes with nitrogen-heterocyclic ligands and showed that the Cu $2p_{3/2}$ binding energies (932.5-932.9 eV) of the Cu^I complexes were ca. 2.5 eV lower than those (935.2–935.4 eV) of the corresponding Cu^{II} complexes. The authors reported also that the Cu $2p_{3/2}$ peak was located at 932.9 eV for Cu(taab)NO3 and at 935.4 eV for $Cu(taab)(NO_3)_2$. On the basis of these data, they concluded that the former copper chelate may be formulated as [Cu¹(taab⁰)]⁺ rather than $[\hat{Cu}^{III}(taab^{2-})]^+$. The main Cu $2p_{3/2}$ peak of 1 was present at practically the same binding energy as that of Cu-(taab)NO₃. Accordingly, the majority of the copper atoms of 1 are in the Cu^I state. The binding energy of the shoulder is almost the same as that of $Cu(taab)(NO_3)_2$. Furthermore, the spectrum showed the shakeup satellites characteristic of Cu^{II} species.²⁰ These results suggest that 1 is a mixed-valence complex involving Cu¹ and Cu¹¹ species.

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Figure 4. Molar magnetic susceptibility χ (in emu) plotted against reciprocal temperature 1/T: Cu(taab)(TCNQ)₂ (A) and Cu(taab)-(TCNQ)_{1.5} (B).

The Cu $2p_{3/2}$ peak of **2** was located at practically the same binding energy as that of Cu(taab)NO₃. The peak was asymmetric with a tail at the high binding energy side and an ill-defined shakeup satellite. Therefore, this compound also involves Cu^I and Cu^{II} species, the former being predominant.

Magnetic Susceptibilities. The molar magnetic susceptibilities were determined on the basis of the molecular weight of each compound formula Cu(taab)(TCNQ)_n that involves one odd electron: 0.79×10^{-3} emu mol⁻¹ for 1 and 0.54×10^{-3} emu mol⁻¹ for 2 at 300 K. These values are much smaller than the susceptibility 1.25×10^{-3} emu mol⁻¹ predicted for the free spin system. Figure 4 shows that the variation of the susceptibilities χ with temperature T follows the equation

$$\chi = \alpha + \gamma / T \tag{6}$$

Here α denotes a temperature-independent paramagnetism and γ/T is the Curie term. The parameters were determined as $\alpha = 0.56 \times 10^{-3}$ emu mol⁻¹ and $\gamma = 0.075$ emu K mol⁻¹ for 1, and $\alpha = 0.50 \times 10^{-3}$ emu mol⁻¹ and $\gamma = 0.014$ emu K mol⁻¹ for 2. The temperature dependence given by eq 6 has been observed for some highly conducting CuL_n(TCNQ)₂ complexes.^{1,18} In these complexes, the α term arises from unpaired electrons that are delocalized over the TCNQ lattices and the γ/T term is due to unpaired electrons localized on the copper sites.

The magnetic susceptibility of (quinolinium)(TCNQ)₂, one of the well-characterized "organic metals", is equal to 0.5×10^{-3} emu mol⁻¹ at room temperature and is practically temperature independent except for very low temperatures.²¹ This paramagnetism probably arises from conduction electrons delocalized over the TCNQ lattices.²¹ The α values of 1 and 2 are nearly equal to the susceptibility of the quinolinium salt. This suggests that TCNQ unpaired electrons are extensively delocalized also in these complexes, although a relation between electric conduction and temperature-independent paramagnetism is not clear for organic metals.

The γ/T term observed for 1 and 2 is an intrinsic property of the complexes, because the ESR signal due to paramagnetic contaminants (i.e., free Cu²⁺ or TCNQ⁻⁻ ions) was not detected. The solid-state equilibrium given by eq 3 results in a fractional spin density distribution on each copper site. This spin delocalization on the copper sites is responsible for the γ/T term, when magnetic interaction between the resulting paramagnetic copper site and its neighboring paramagnetic species is very weak compared with the thermal energy. The spin system in which one odd electron exists on each magnetic site shows the Curie-type paramagnetism given by eq 5. The ratio of γ to the Curie constant 0.375 of eq 5 gives the unpaired electron density residing on each copper atom: 0.2 for 1 and 0.04 for 2. Some charge-transfer complexes contain a significant number of crystal defects such as chain ends, which show the Curie-type paramagnetic behavior. For this reason, the Cu spin densities evaluated from the γ values may be overestimated. This magnetic study, however, affords additional evidence for the mixed-valence state of copper.

Electric Conduction. From a steric requirement, the taab ligand has a saddle-shaped structure.²² This nonplanarity of the rather bulky ligand is unfavorable to intermolecular charge-transfer interaction. In fact, a partially oxidized Pd complex, Pd- $(taab)(I_3)_{2.7},$ is a poor conductor with $10^{-8}\;S\;cm^{-1.23}$. The high electric conduction in 1 and 2, therefore, is undoubtedly due to the TCNQ moieties. Structural information is not available, because single crystals have not been obtained. We can, however, reasonably assume the presence of TCNQ columns, each separated by Cu(taab) stacks. This type of segregated column structure has been found commonly for a number of highly conducting TCNQ complexes:²⁴ this is one of the important features of organic metals. Our magnetic susceptibility study provided evidence for the proposed structure: (1) the unpaired electrons of TCNQ^{•-} are extensively delocalized and are coupled strongly with each other and (2) the magnetic interaction between the copper chelate and TCNQ is very weak compared with the thermal energy.

Each TCNQ in $[Cu^{I}(taab)][(TCNQ)_{n}]^{\bullet-}$ carries a mean fractional charge, -1/n, which results in the formation of current carriers in the TCNQ lattices. The fractional charge occupation is the result of the redox reaction between Cu^{II}(taab) and TCNQ^{•-} (eq 1). The successive back-electron transfer given by eq 3 may cause a fluctuation of the TCNQ charge density to facilitate charge propagation in the lattices. Thus, the Cu(taab) chelate plays an indirect but important role for electric conduction. This is evident when compared with the electrical property of a Cu-TCNQ complex with an aliphatic macrocyclic ligand, 1,4,8,11tetraazacyclotetradecane (abbreviated as cyclam). The copper(II) chelate of this ligand was reported to form [Cu^{II}(cyclam)]- $(\text{TCNQ}^{\bullet-})_2 \cdot 2\text{H}_2\text{O}$, whose powder conductivity was $1.8 \times 10^{-7} \text{ S}$ cm⁻¹ at room temperature.²⁵ In the course of the formation of this complex, a redox reaction does not occur between Cu^{II}(cyclam) and TCNQ.: each TCNQ of the resulting complex carries -1 charge.26

The mechanism of the stabilization of the d¹⁰ configuration of copper in [Cu(taab)]⁺ is not clear. A structural study of Ni^{II}(taab) complexes showed that four nitrogen atoms of the Ni(II) chelate lie on a saddle-shaped surface with a deviation of ca. 0.2 Å out of the mean plane of Ni–N₄.²² This small tetragonal distortion may contribute to the stabilization of the d¹⁰ configuration. A back-donation from Cu^I to taab through π overlap also may stabilize [Cu^I(taab)]⁺. In fact, the coordination of cyclam that is an aliphatic ligand does not stabilize the Cu^I state as described above.

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⁽²⁶⁾ The CH bending frequency of TCNQ was observed at 828 cm⁻¹ for this compound in our present study. This data supports the formula which involves $TCNQ^{-}$.