

(c) TSPcFe^{II} is known to be water-soluble. Thus, it appears improbable that it can be precipitated from 96% H₂SO₄ by dilution with water and isolated as a solid after repeated washings necessary for the removal of excess of acidity,^{1b} also because acidity would be an intrinsic property of the suggested material.

(d) No bands of the SO₃H groups are present in the expected region of the IR spectrum reported.⁶

Conclusions. (PcFe)₂O represents, to our knowledge, a unique example of a μ -oxo-bridged Fe(III) porphyrin-like molecule for which two solid crystalline isomers have been isolated and characterized. μ -Oxo(1) and μ -oxo(2) show different X-ray powder patterns, IR and Mössbauer spectra, and magnetic susceptibility behavior. Both of them are strongly antiferromagnetically coupled Fe(III) high-spin dimeric systems ($S = 5/2$). The higher J value found for μ -oxo(2) (-195 cm^{-1}) with respect to that of μ -oxo(1) ($J = -120 \text{ cm}^{-1}$; bent Fe-O-Fe moiety) is suggestive of a linear or quasi-linear Fe-O-Fe bond system, in keeping with the available crystallographic information. Finally, although μ -oxo(2) has very likely an intermediate structure between that of high-spin five-coordinate μ -oxo(1) and that of low-spin [(py)PcFe]₂O, it still shows a high-spin ($S = 5/2$) ground state, very likely associated with a retained essentially five-coordinate environment with very weak or insignificant axial external contacts for Fe(III).

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Note Added in Proof. While the present paper was in press, we learned of a recent report on (PcFe)₂O referring to Frampton and Silver's work⁶ and to ours¹ on the same subject (see ref 24, as well as ref 25, a previous report by the same author). In a reevaluation of mostly previously published material, the author seems to support the existence of two Fe(III)-containing crystalline materials, as clearly established by us previously.^{1b} The two isomers are renamed FePcoxyg₁ (i.e. μ -oxo(1)) and FePcoxyg₂ (i.e. μ -oxo(2)) (previously identified as S and B species, respectively,²⁵ S being changed into P and a mysterious imidazole derivative of P being labeled M in a later short report by the same author²⁶), with little gain, throughout the paper, from the point of view of the exact chemical formulation of the species and no contribution to the clarification of the molecular and electronic structure of the two individual isomers. For other marginal details these reports²⁴⁻²⁶ will be eventually referred to elsewhere.

Registry No. μ -oxo(2), 74353-48-3.

(24) Collamati, I. *Inorg. Chim. Acta* **1986**, *124*, 61-66.

(25) Collamati, I. *Inorg. Chim. Acta* **1979**, *35*, L303-L304.

(26) Collamati, I. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 69-73.

Contribution from the Centro de Investigación en Polímeros y Materiales, Universidad de Sonora, Hermosillo, Sonora, Mexico, and Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Highly Electroconductive Tetrathiafulvalenium Salts of Copper Halides

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The redox reaction of copper(II) halides with excess tetrathiafulvalene (TTF) yielded a variety of electroconductive mixed-valence complexes in different solvents: (TTF)₂CuCl₂ (the powder electrical conductivity was 14 S cm⁻¹ at 300 K) in methanol, (TTF)₇(CuCl₂)₃ (10 S cm⁻¹) in acetonitrile, (TTF)₅(CuBr₂)₃ (1.5 S cm⁻¹) in methanol, (TTF)₄(CuBr₂)₃ (0.3 S cm⁻¹) in tetrahydrofuran, and (TTF)₆CuBr₄ (14 S cm⁻¹) in acetonitrile. Electron spin resonance, infrared, and X-ray photoelectron spectroscopic studies indicated that, in each compound, the copper atoms are in the Cu^I state and TTF moieties carry a fractional charge equally. The magnetic susceptibilities suggested that unpaired electrons are extensively delocalized over the TTF lattices.

Introduction

Tetrathiafulvalene (TTF) and its analogues have been found to form highly electroconductive donor-acceptor complexes.^{2,3} Their electrical properties can be varied over a wide range by changing the nature of the acceptor species. The use of metal chelates as acceptors is expected to be a versatile route for the preparation of a wide variety of conductive TTF complexes that exhibit different electrical properties, because various types of metal chelate anions can be employed with different geometries and oxidation states of the central metal ion. On this basis, several metal complexes involving TTF or its analogues have been prepared.⁴ An important compound that has been prepared recently

is (BEDT-TTF)₂AuI₂ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene), which undergoes a transition to a superconducting state at ca. 5 K.⁵

One of the common features of the conducting donor-acceptor complexes is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.^{2,3,6} Accordingly, the preparation of conductive TTF complexes requires the use of appropriate oxidants that can oxidize TTF⁰ partially to TTFⁿ⁺ ($n < 1$). Copper(II) chelates are expected to function as oxidants with respect to TTF⁰ under appropriate conditions, because they have low standard-electrode-potential values and are readily converted to the corresponding Cu^I chelates.⁷ Copper(II) halides have been reported to oxidize TTF⁰ readily to TTF⁺ or TTF²⁺,^{8,9} the resulting

(1) (a) Universidad de Sonora. (b) University of Arizona.

(2) "Proceedings of the International Conference on Low-Dimensional Conductors", *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 85, 86.

(3) "Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals", *Mol. Cryst. Liq. Cryst.* **1985**, *119*, 120.

(4) (a) Interrante, L. V.; Browall, K. W.; Hart, H. R., Jr.; Jacobs, I. S.; Watkins, G. D.; Wee, S. H. *J. Am. Chem. Soc.* **1975**, *97*, 889. (b) Wudl, F. *J. Am. Chem. Soc.* **1975**, *97*, 1962. (c) Kistenmacher, T. J.; Rossi, M.; Chiang, C. C.; Van Duyne, R. P.; Cape, T.; Siedle, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 1958. (d) Kondo, K.; Matsubayashi, G.; Tanaka, T.; Yoshioka, H.; Nakatsu, K. *J. Chem. Soc., Dalton Trans.* **1984**, 379.

(5) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nuñez, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2465.

(6) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(7) Meites, L.; Zuman, P.; Narayanan, A.; Fenner, T. L.; Jandík, J. *CRC Handbook Series in Inorganic Electrochemistry*; CRC: Boca Raton, FL, 1981; Vol. II.

(8) Siedle, A. R.; Candela, G. A.; Finnegan, T. F.; Van Duyne, R. P.; Cape, T.; Kokoszka, G. F.; Woyciejes, P. M.; Hashmall, J. A. *Inorg. Chem.* **1981**, *20*, 2635.

(9) Honda, M.; Katayama, C.; Tanaka, J.; Tanaka, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41C*, 197.

Table I. Physical Properties of TTF-Cu Complexes: Electrical Powder Conductivity σ ($S\text{ cm}^{-1}$) at 300 K, Thermoelectric Power Q ($\mu\text{V K}^{-1}$), Magnetic Susceptibility χ (emu mol^{-1}) per Compound Formula at 300 K, ESR g Value, and Wavenumber (cm^{-1}) of the IR ν_{16} Band^a

	σ	Q	$10^4\chi$	g	ν_{16}
(TTF) _{7/3} CuCl ₂	10	30	3.2	2.006 ₅	815
(TTF) ₂ CuCl ₂	14	35	3.3	2.006 ₃	816
(TTF) _{5/3} CuBr ₂	1.5	30	1.3	2.006 ₅	825
(TTF) _{4/3} CuBr ₂	0.3	10	0.5	2.007 ₉	830
(TTF) ₆ CuBr ₄	14	10	1.5 ^b	2.006 ₇	825 ^c

^a For the numbering of the mode, see ref 20. ^b Determined on the basis of the formula (TTF)₂(CuBr₄)_{1/3}, which involves one unpaired electron. ^c Not determined accurately.

complexes, however, are poorly electroconductive. Recently, we have reported that copper(II) chloride oxidizes TTF⁰ partially under appropriate conditions to yield a mixed-valence complex, [(TTF)₂]^{•+}Cu^ICl₂, whose powder conductivity exhibits quasi-metallic temperature dependence above ca. 250 K.¹⁰ The reduction potential of the metal ion is influenced by a variety of solution parameters such as solvation⁷ and can, therefore, assume a wide range of values. In this paper, we report that the use of different solvents results in the formation of different TTF complexes with copper halides. The complexes have been characterized with the aid of electron spin resonance (ESR), infrared (IR), and X-ray photoelectron spectroscopies and magnetic susceptibility measurements.

Results

Complex Formation. (TTF)₂CuCl₂ was obtained by adding a methanol solution of CuCl₂·2H₂O to excess TTF dissolved in the same solvent.¹⁰ The composition was independent of the TTF:CuCl₂·2H₂O ratio in the reaction as long as TTF was used in excess. When acetonitrile was employed as the solvent instead of methanol, (TTF)₇(CuCl₂)₃ was obtained independent of the TTF:CuCl₂·2H₂O ratio in the reaction mixture. The TTF salts of copper bromide were prepared by the use of CuBr₂ in place of the chloride. The composition of the bromides, however, was different from that of the corresponding chlorides: (TTF)₅(CuBr₂)₃ was separated in methanol, (TTF)₄(CuBr₂)₃ in tetrahydrofuran,¹¹ and (TTF)₆CuBr₄ in acetonitrile. The difference between the chlorides and bromides arises obviously from the difference in the stabilization of the Cu^I state in the solvents.

Electrical Properties. Every compound exhibited high powder conductivity and small positive thermoelectric power as shown in Table I. Figure 1 shows the temperature dependence of the powder conductivities. As reported in our previous paper,¹⁰ (TTF)₂CuCl₂ exhibited temperature-independent (i.e., quasi-metallic) conductivity above ca. 250 K. At low temperatures, the variation of the conductivity σ with temperature T is given by

$$\sigma = \sigma_{\infty} e^{-E/kT} \quad (1)$$

which is characteristic of intrinsic semiconductors. The activation energy E was found to be ca. 0.07 eV. This is indicative of the occurrence of a metal-semiconductor transition. (TTF)_{5/3}CuBr₂ showed thermally activated conductivity as given by eq 1 with $E = 0.049$ eV in the temperature range investigated. The conductivities of (TTF)_{7/3}CuCl₂ and (TTF)₆CuBr₄ exhibited complicated temperature dependence. The $\ln \sigma$ vs. $1/T$ plot observed for each of the two compounds has an inflection point at ca. 160 K and reaches an asymptote at both the high- and the low-temperature limits. From the asymptote of the high-temperature limit, the activation energy can be calculated approximately; it is 0.03 eV for (TTF)_{7/3}CuCl₂ and 0.04 eV for (TTF)₆CuBr₄. These values are comparable with the energy predicted for contact resistance between powder particles; the intrinsic conductivities may be

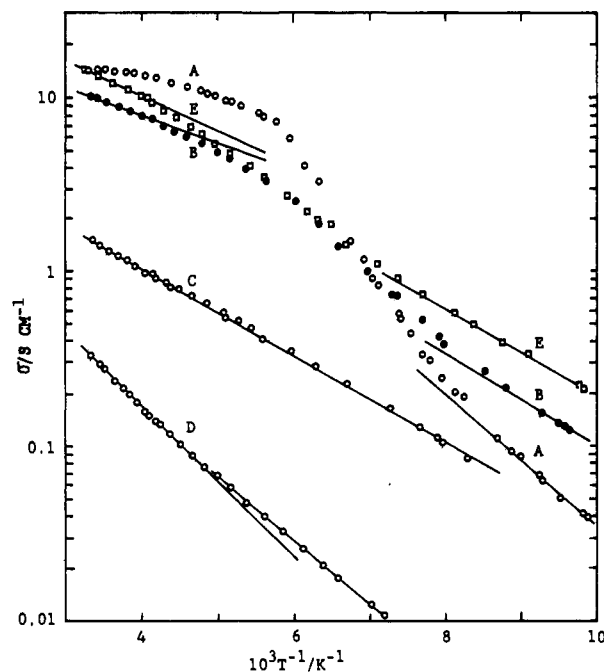


Figure 1. Electrical powder conductivities, σ , plotted against reciprocal temperature, T^{-1} , for (TTF)₂CuCl₂ (A), (TTF)_{7/3}CuCl₂ (B), (TTF)_{5/3}CuBr₂ (C), (TTF)_{4/3}CuBr₂ (D), and (TTF)₆CuBr₄ (E). The straight lines show $\sigma = \sigma_{\infty} e^{-E/kT}$ (see text for the respective activation energies, E).

metallic. The asymptote of each compound at the low-temperature limit gives an activation energy of 0.05 eV, which is significantly larger than that at the high-temperature limit. A change in the conduction mechanism occurs in the vicinity of the inflection point. The $\ln \sigma$ vs. $1/T$ curve observed for (TTF)_{4/3}CuBr₂ is given by eq 1 with $E = 0.085$ eV above ca. 210 K and with $E = 0.071$ eV below this temperature. These data suggest that the conduction mechanism changes at ca. 210 K. An alternative explanation is that the electric conduction is governed by the variable-range hopping of electrons; the conductivity is given by¹²

$$\sigma = A e^{-(8/kT)^{1/4}} \quad (2)$$

This equation explains the temperature variation of the conductivity of (TTF)_{4/3}CuBr₂ fairly well throughout the temperature range investigated. Unfortunately, we cannot choose between the two models. In any event, this compound does not appear to have metal-like properties.

ESR Spectra. All the compounds gave a single symmetric ESR spectrum with a peak-to-peak width of 1.1–1.6 mT. The observed g values are nearly equal to 2.00838 for TTF^{•+} radicals in solution¹³ (Table I); the ESR signal arises from unpaired electrons distributed on TTF. A signal attributable to Cu^{II} ions was not detected in the spectra; the copper atoms in each compound are in the diamagnetic Cu^I state. Therefore, the (TTF) _{n} CuX₂-series compounds can be formulated as [(TTF) _{n}]^{•+}Cu^IX₂, and (TTF)₆CuBr₄ as [(TTF)₆]^{3•+}Cu^IBr₄.

Sulfur radicals in which unpaired electrons are localized on sulfur atoms have a g value nearly equal to 2.03, which is much larger than the value 2.003 of carbon radicals, because of the large spin-orbit coupling constant of sulfur.¹⁴ The g value of TTF^{•+} radicals depends on the spin density on the sulfur atoms.¹⁵ The g values observed for the TTF-Cu complexes are slightly smaller than the value of 2.00838 for TTF^{•+} in solution,¹³ whereas a large

(10) Inoue, M.; Inoue, M. B. *J. Chem. Soc., Chem. Commun.* **1985**, 1043.

(11) The chloride prepared by the use of tetrahydrofuran as solvent had the composition (TTF)₂CuCl₂, and its physical and spectroscopic properties closely resemble those of the chloride prepared by the use of methanol.

(12) Mott, N. F. *Metal-Insulator Transitions*; Taylor & Francis: London, 1974.

(13) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453.

(14) Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Free Radicals*; Academic: New York, 1968; p 352.

(15) Kinoshita, N.; Tokumoto, M.; Anzai, M.; Ishiguro, T.; Yamabe, T.; Teramae, H.; Saito, G. *Mol. Cryst. Liq. Cryst.* **1985**, *119*, 221.

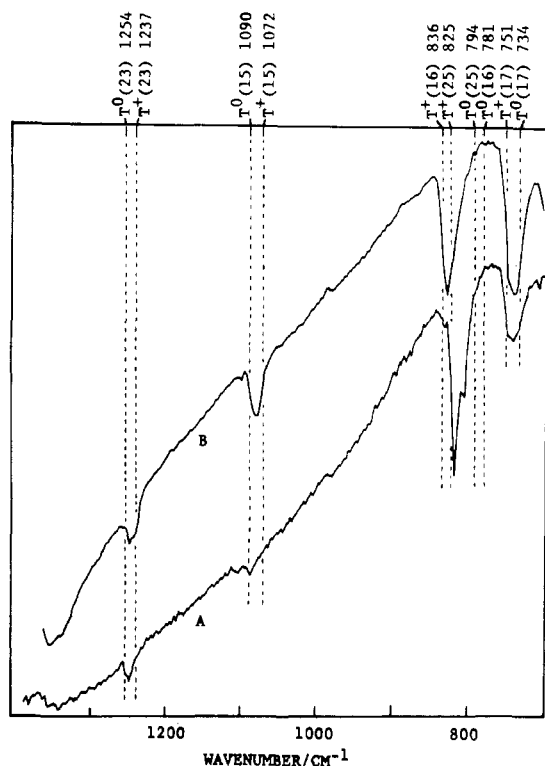


Figure 2. IR spectra of $(\text{TTF})_2\text{CuCl}_2$ (A) and $(\text{TTF})_{4/3}\text{CuBr}_2$ (B). At the top, the wavenumbers of the vibrational bands are shown for TTF^0 (abbreviated as T^0) and TTF^{++} (T^+). The numbering of the vibrational modes is given in parentheses and follows that used in ref 20.

g value of 2.013 has been reported for $(\text{TTF})\text{I}_{0.71}$.¹⁶ This is an example that demonstrates that the spin density distribution in TTF may be influenced to a great extent by environmental effects such as intermolecular forces. In the TTF-Cu complexes, one unpaired electron is shared by TTF molecules in each $[(\text{TTF})_n]^{++}$ unit: the mean unpaired electron number residing on TTF is equal to $+1/n$. The complexes have essentially the same g value; they have the same spin density distribution within a TTF moiety, although the total spin density (i.e., mean unpaired electron number) of TTF is different from one compound to another.

IR Spectra. All the $(\text{TTF})_n\text{CuX}_2$ -type compounds showed a very broad intense band extending from the near IR region to a band edge at ca. 1200 cm^{-1} . A similar band has been observed for many conducting TCNQ complexes,^{17,18} and has been interpreted on the basis of an electronic transition.¹⁹ Probably the same type of electronic absorption also appears in the IR spectra of the TTF complexes. Four vibrational bands of TTF were observed in the absorption tail. The spectra of $(\text{TTF})_2\text{CuCl}_2$ and $(\text{TTF})_{4/3}\text{CuBr}_2$ are shown in Figure 2 as typical examples.

The transmittance of $(\text{TTF})_6\text{CuBr}_4$ was very low all throughout the $4000\text{--}700\text{ cm}^{-1}$ region, and consequently, the vibrational bands of this compound were difficult to identify unequivocally. An electronic absorption band probably extends over a region below 700 cm^{-1} . Only a very weak band was observed at ca. 825 cm^{-1} .

IR assignments have been made for TTF^{++} ions as well as for TTF^0 molecules.²⁰ A comparison of the results with the observed spectra of $(\text{TTF})_n\text{CuX}_2$ leads to assignments that are shown in Figure 2: the 1245-cm^{-1} band is assigned to the ν_{23} mode (contributed mainly from CCH bend), the 1085-cm^{-1} band to ν_{15} (CCH bend), and the 740-cm^{-1} band to ν_{17} (CS stretch). The ν_{16} (CS stretch) and ν_{25} (ring SCC bend) modes of TTF^{++} and

of TTF^0 appear in a region of $780\text{--}840\text{ cm}^{-1}$, and the former band is more intense than the latter.²⁰ The band observed at ca. 820 cm^{-1} in each spectrum can be assigned to the ν_{16} mode; the ν_{25} band is probably masked by the ν_{16} band. A shoulder observed at 805 cm^{-1} in the spectrum of $(\text{TTF})_2\text{CuCl}_2$ may be assigned to the ν_{25} mode.

The vibrational modes of constituent molecules in charge-transfer complexes show a frequency shift that is dependent on the charge occupation of the molecules. This ionization shift is well understood for the TCNQ and chloranil anion radicals, and arises from the variation of bond orders upon ionization.²¹ Some vibrational bands of TCNQ shift in a linear manner with the charge occupation in TCNQ. This relation has been employed for the evaluation of the charge density residing on TCNQ in its mixed-valence complexes.¹⁸ The correlation between bond order and force constant has been pointed out to be less straightforward in TTF than in TCNQ.²⁰ Despite this ambiguity, the ν_{16} mode has an apparently large ionization shift.²⁰ The wavenumber of the mode observed for $(\text{TTF})_n\text{CuX}_2$ is dependent on the compound as shown in Table I. The observed wavenumber can be related to the value of n in the compound formula by the following equation within $\pm 2\text{ cm}^{-1}$:

$$\nu_{16} = 792 + 51/n \text{ (cm}^{-1}\text{)} \quad (3)$$

When n constituents of TTF in $[(\text{TTF})_n]^{++}\text{Cu}^1\text{X}_2$ share +1 charge equally, $1/n$ gives the mean charge residing on TTF. The frequency shift of the ν_{16} mode, therefore, can be interpreted in terms of the ionization effect. The above equation yields the extreme values 792 cm^{-1} for $1/n = 0$ and 843 cm^{-1} for $1/n = 1$, which are slightly higher than the values 781 cm^{-1} observed for TTF^0 in solution and 836 cm^{-1} for $(\text{TTF})^{++}\text{Br}^-$, respectively.²⁰ This disagreement is due to environmental effects: strictly speaking, the linear relation between wavenumber and charge occupation holds for a series of complexes in which the intermolecular interactions are similar.²⁰ In view of this limitation, the above interpretation of the frequency shift is very reasonable. This affords evidence that supports the formula $[(\text{TTF})_n]^{++}\text{Cu}^1\text{X}_2$, in which n constituents of TTF share +1 charge equally.

The weak 825-cm^{-1} band of $(\text{TTF})_6\text{CuBr}_4$ can be assigned to the ν_{16} mode. The wavenumber calculated from eq 3 on the basis of the formula $[(\text{TTF})_6]^{3++}\text{Cu}^1\text{Br}_4$ was 818 cm^{-1} . In view of the above-mentioned limitation of eq 3, the agreement is reasonable. Each TTF carries a fractional charge equally in this compound.

X-ray Photoelectron Spectra. The copper $2p_{3/2}$ -core electron peak was found at 932.9 eV for $(\text{TTF})_{7/3}\text{CuCl}_2$, 933.0 eV for $(\text{TTF})_2\text{CuCl}_2$, 932.7 eV for $(\text{TTF})_{5/3}\text{CuBr}_2$, 932.2 eV for $(\text{TTF})_{4/3}\text{CuBr}_2$, and 932.4 eV for $(\text{TTF})_6\text{CuBr}_4$. The full width at half-maximum height (FWHM) of each peak was equal to 2.7 eV . The Cu $2p_{1/2}$ peaks were located at an energy 20.0 eV higher than that of the corresponding $2p_{3/2}$ peaks. The observed values of the binding energies are reasonable for Cu^1 species.^{22,23} Furthermore, the shake-up satellites, which are characteristic of the Cu^{II} state,²⁴ were not present in each spectrum. These results clearly show that the copper atoms of the compounds are in the Cu^1 state.

The binding energies of the sulfur $2p$ peaks were between 164.1 and 164.5 eV . Each peak was slightly asymmetric with a tail at the high-binding-energy side, and the FWHM was equal to ca. 2.9 eV . Ikemoto, et al.²⁵ reported that the S $2p$ spectra of the mixed-valence TTF halides $(\text{TTF})\text{Br}_{0.7}$ and $(\text{TTF})\text{I}_{0.7}$ were significantly broader (FWHM = $2.7\text{--}3.1\text{ eV}$) than those of TTF^0 (FWHM = 2.1 eV) and TTF^{++} (FWHM = 2.5 eV). The authors resolved the S $2p$ spectrum of each compound to TTF^0 and TTF^{++}

- (16) Sugano, T.; Kuroda, H. *Chem. Phys. Lett.* **1977**, *47*, 92.
 (17) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
 (18) Inoue, M.; Inoue, M. B. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 539 and references therein.
 (19) Rice, M. J.; Pietronero, L.; Brüesch, P. *Solid State Commun.* **1977**, *21*, 757.
 (20) Bozio, R.; Zanon, I.; Girlando, A.; Pecile, C. *J. Chem. Phys.* **1979**, *71*, 2282. The modes are numbered after this reference.

- (21) (a) Girlando, A.; Zanon, I.; Bozio, R.; Pecile, C. *J. Chem. Phys.* **1977**, *68*, 22. (b) Bozio, R.; Zanon, I.; Girlando, A.; Pecile, C. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1237.
 (22) Brant, P.; Fernando, Q. *J. Inorg. Nucl. Chem.* **1978**, *40*, 235.
 (23) Gagné, R. P.; Allison, J. L.; Koval, C. A.; Mialki, W. S.; Smith, T. J.; Walton, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1905.
 (24) Frost, D. C.; Ishitani, A.; McDowell, C. A. *Mol. Phys.* **1972**, *24*, 861.
 (25) Ikemoto, I.; Yamada, M.; Sugano, T.; Kuroda, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1871.

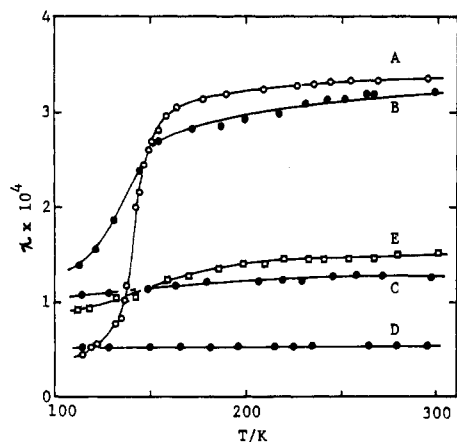


Figure 3. Temperature dependence of molar magnetic susceptibilities, χ , (in emu) of $(\text{TTF})_2\text{CuCl}_2$ (A), $(\text{TTF})_{7/3}\text{CuCl}_2$ (B), $(\text{TTF})_{5/3}\text{CuBr}_2$ (C), $(\text{TTF})_{4/3}\text{CuBr}_2$ (D), and $(\text{TTF})_6\text{CuBr}_4$ (E). The curves are drawn to aid the view.

components and demonstrated the mixed-valence state of the TTF moiety. The S 2p spectra observed for the TTF-Cu complexes were difficult to resolve into two component peaks. The large value of the FWHM, however, is practically the same as that of the mixed-valence TTF halides and probably arises from the overlap of the TTF^0 and TTF^{2+} components. This, together with the Cu 2p spectra, supports the formulations proposed by our ESR and IR studies.

Magnetic Susceptibilities. Table I summarizes the room-temperature molar susceptibilities determined on the basis of the compound formula that involves one odd electron. The magnetic susceptibilities of $(\text{TTF})_{5/3}\text{CuBr}_2$ and $(\text{TTF})_{4/3}\text{CuBr}_2$ were practically temperature-independent over the temperature range investigated. Other complexes exhibited temperature-independent susceptibility at high temperatures, but a relatively large variation was observed at low temperatures, as shown in Figure 3.

Because of the apparent low nucleophilicity of the TTF sulfur, strong metal-sulfur coordination bonds are difficult to form.⁸ The TTF molecules of the TTF-Cu complexes may form one-dimensional columns without being coordinated to copper: TTF columns, each separated by anion columns, are commonly found for highly conducting TTF complexes.^{2,3} The presence of TTF columns in the TTF-Cu complexes is supported by the observed weak temperature-independent paramagnetism, which is due to strong magnetic interactions operative between $(\text{TTF})_n$ units: the magnetism can be interpreted in terms of electrons delocalized extensively over infinite spin lattices.

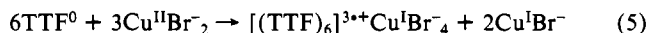
$(\text{TTF})_2\text{CuCl}_2$ exhibited a magnetic anomaly due to the phase transition that was found in the $\ln \sigma$ vs. $1/T$ plot: around 160 K, the Pauli-type paramagnetism was changed abruptly to diamagnetism in the low-temperature semiconducting state. The magnetic susceptibility of $(\text{TTF})_{7/3}\text{CuCl}_2$ also sharply decreased with decreasing temperature below ca. 160 K. This temperature is nearly the same as that of the inflection point found in the $\ln \sigma$ vs. $1/T$ plot. Thus, the magnetic susceptibility is also indicative of the occurrence of a phase transition.

Discussion

The spectroscopic studies have consistently demonstrated that the formation of $(\text{TTF})_n\text{CuX}_2$ accompanies the following incomplete redox reaction:



In acetonitrile, a different type of reaction occurs between TTF and CuBr_2 , probably due to the high stability of copper(I) bromide species:



Because TTF readily forms nonstoichiometric compounds in its direct oxidation with acceptors such as Cl_2 and Br_2 , the composition of the complexes is somewhat troublesome to control.²⁶

Table II. Analytical Data

	solvent	anal., % found (calcd)			
		C	H	Cl, Br	Cu
$(\text{TTF})_2\text{CuCl}_2$	CH_3OH	27.12 (26.54)	1.55 (1.48)	12.78 (12.05)	11.5 (11.7)
$(\text{TTF})_{7/3}(\text{CuCl}_2)_3$	CH_3CN	27.22 (27.51)	1.53 (1.54)	11.52 (11.60)	9.6 (10.4)
$(\text{TTF})_5(\text{CuBr}_2)_3$	CH_3OH	21.60 (21.30)	1.26 (1.19)	27.87 (28.34)	11.5 (11.3)
$(\text{TTF})_4(\text{CuBr}_2)_3$	THF^a	19.11 (19.38)	1.08 (1.11)	31.69 (32.23)	13.7 (12.8)
$(\text{TTF})_6\text{CuBr}_4$	CH_3CN	26.56 (26.87)	1.51 (1.50)	19.01 (19.86)	4.1 (3.9)

^a THF: tetrahydrofuran. The chloride prepared by using this solvent had the composition $(\text{TTF})_2\text{CuCl}_2$.

In the preparation of the TTF-Cu complexes, however, the composition of the materials can be controlled precisely and readily by use of appropriate solvents. The composition is dependent only on the kind of solvent employed and is independent of other reaction conditions such as the TTF: CuX_2 ratio, as long as the TTF is in excess. The exact control of the composition is performed by the effect of solvation on the redox potential of copper(II) halides. Siedle et al.⁸ studied reactions between TTF and excess copper(II) halides and obtained quite different compounds: for example, $(\text{TTF}^{2+})\text{Cu}^{\text{II}}\text{Cl}_4$ was formed by the addition of TTF to a large excess of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acetonitrile. The results of the two extreme reaction conditions can be understood in a straightforward manner: in the reaction system containing CuCl_2 and excess TTF, TTF^{+} that is initially formed reacts with TTF^0 to form $[(\text{TTF})_{7/3}]^{+}\text{Cu}^{\text{I}}\text{Cl}_2$, but in the system containing an excess of CuCl_2 , TTF^{+} is oxidized further to TTF^{2+} by excess Cu^{2+} ions. The use of excess TTF is considered to be essential for the preparation of the conductive TTF complexes, because the presence of a fractional charge on TTF is required for high electric conduction.

The materials obtained in the present study are stable in air, despite the presence of Cu^{I} species in the complexes. Our XPS study indicated that the samples were not contaminated with Cu^{II} species even on the surface, although the sample-handling for XPS was carried out in air.

Each TTF molecule in the complexes formed has a fractional positive charge so that positive holes are produced in the TTF lattices. The resulting positive holes carry the high electric current in the complexes. This is consistent with the positive thermoelectric power observed for the complexes (Table I). Copper halide anions do not contribute directly to the electric conduction, but they may play an important role in the stabilization of the mixed-valence state of TTF and in the formation of the current carriers in the TTF lattices.

In our previous papers,²⁷ we reported that the use of copper(II) chelates is a versatile method for the preparation of different types of electroconductive TCNQ complexes. The present investigation has demonstrated that copper(II) halides can function as excellent acceptors with respect to TTF to form highly electroconductive complexes. The use of different copper(II) compounds is expected to yield varying types of conducting TTF complexes.

Experimental Section

Materials. Sublimed grade TTF and 99.999% pure (metal basis) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, both supplied from Strem, were used without further purification. Reagent grade CuBr_2 was used after recrystallization. Spectroscopic grade methanol and acetonitrile (Merck) were used as supplied. Tetrahydrofuran (THF) was distilled over sodium metal before use.

All the TTF-Cu complexes were prepared by essentially the same procedure: the addition of a copper(II) halide to excess TTF in an

(26) Scott, B. A.; La Placa, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* **1977**, *99*, 6631.

(27) (a) Inoue, M.; Inoue, M. B.; Seto, T.; Nakamura, D. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 139. (b) Inoue, M.; Inoue, M. B. *Inorg. Chem.* **1986**, *25*, 37.

appropriate solvent. The materials obtained and the solvents employed are summarized in Table II together with the analytical data. Elemental analyses except for copper were performed by Huffman Laboratories, Wheatridge, CO. The materials were stable enough to be handled in air. As long as TTF was in excess, the composition of the materials obtained was independent of reaction conditions, such as the TTF:CuX₂ ratio. A typical method of preparation of each of the materials is described below.

(TTF)₂CuCl₂. A solution of 11 mg (0.065 mmol) of CuCl₂·2H₂O in 1.5 mL of methanol was added with stirring to 29 mg (0.14 mmol) of TTF dissolved in 3 mL of methanol under a nitrogen atmosphere. Deep purple crystalline powders were formed. After the resulting mixture was stirred for ca. 1 h, the precipitate was collected on a filter, washed with ethanol, and dried under vacuum.

(TTF)₇(CuCl₂)₃. An acetonitrile solution of CuCl₂·2H₂O (0.076 mmol in 2.5 mL) was added with stirring to TTF (0.177 mmol) dissolved in acetonitrile (2.5 mL) under a nitrogen atmosphere. After the resulting mixture was stirred for ca. 1 h, the precipitate formed was collected on a filter, washed with acetonitrile, and dried under vacuum.

(TTF)₅(CuBr₂)₃. A methanol solution of CuBr₂ (0.054 mmol in 1 mL) was added with stirring to a methanol solution of TTF (0.111 mmol in 2.5 mL) under a nitrogen atmosphere. After the resulting mixture was stirred for ca. 1 h, the precipitate formed was collected, washed with ethanol, and dried under vacuum.

(TTF)₄(CuBr₂)₃. A tetrahydrofuran (THF) solution of CuBr₂ (0.078 mmol in 5 mL) was added with stirring to TTF (0.16 mmol) dissolved in THF (2.5 mL) under a nitrogen atmosphere. After the resulting mixture was stirred for ca. 1 h, the precipitate formed was collected on a filter, washed with THF, and dried under vacuum.

(TTF)₆CuBr₄. An acetonitrile solution of CuBr₂ (0.072 mmol in 1 mL) was added with stirring to 0.156 mmol of TTF dissolved in acetonitrile (2 mL) under a nitrogen atmosphere. The resulting mixture was stirred for ca. 1 h. The precipitate formed was collected on a filter, washed with acetonitrile, and dried under vacuum.

Physical Measurements. The electrical conductivity was determined on the compressed pellets by van der Pauw's 4-probe method²⁸ in a temperature range of 100–300 K. The thermoelectric power of the pellets

was determined against copper metal with platinum contacts at 300 K.

The ESR spectra were recorded by means of a Varian E-3 spectrometer. Diphenylpicrylhydrazyl was employed as a calibrant for determining *g* values.

The IR spectra of the compounds in Nujol mulls were recorded with a Perkin-Elmer 1420 spectrophotometer. The nature of the spectra observed was independent of mull-preparation techniques.

The X-ray photoelectron spectra were obtained with a Vacuum Generators ESCALAB MK II spectrometer (East Grinstead, U.K.). The pressure in the sample chamber did not exceed 5×10^{-10} Torr during the experiments. All samples were irradiated with Al K α X-rays (1486.6 eV). The sample powders were mixed with ultrapure 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. Throughout each of the experiments, no significant outgassing of the samples was detected, and no other indications of sample decomposition were observed. The data were recorded digitally, and all peak scans were signal-averaged until an acceptable signal:noise ratio was obtained.

The magnetic susceptibility was determined by means of a Faraday balance²⁹ in the temperature range 100–300 K. Sodium chloride (-0.52×10^{-6} emu g⁻¹) was used as a calibrant.²⁹ The molar susceptibility was corrected for diamagnetic contributions (10^{-6} emu mol⁻¹) from TTF (-99),³⁰ Cl⁻ (-26), and Br⁻ (-36).³¹

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Registry No. TTF, 31366-25-3; (TTF)₂CuCl₂, 99639-32-4; (TTF)₇(CuCl₂)₃, 104034-45-9; (TTF)₅(CuBr₂)₃, 99639-34-6; (TTF)₄(CuBr₂)₃, 104034-46-0; (TTF)₆CuBr₄, 104034-48-2; CuCl₂, 7447-39-4; CuBr₂, 7789-45-9.

(29) Inoue, M. B.; Inoue, M. *Mol. Cryst. Liq. Cryst.* **1983**, *95*, 183.

(30) Scott, J. C.; Garito, A. F.; Heeger, A. J. *Phys. Rev. B: Solid State* **1976**, *10*, 3131.

(31) Boudreaux, E. A.; Mulay, L. M., Eds. *Theory and Applications of Molecular Paramagnetism*; Wiley: New York, 1976.

(28) van der Pauw, J. L. *Philips Res. Rep.* **1958**, *13*, 1.

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Synthesis and Structure of [Rhodamine 123]₂PtCl₄·4H₂O: The First Tetrachloroplatinate(II) Salt with Anticancer Activity

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The preparation and characterization of bis(Rhodamine 123)tetrachloroplatinate(II) tetrahydrate, [RH(123)]₂PtCl₄·4H₂O (A), is described. Crystals of A are monoclinic C2/c with *a* = 13.318 (3) Å, *b* = 21.702 (5) Å, *c* = 15.485 (3) Å and β = 94.11 (2)° and have four formula units in the unit cell. The structure was determined by standard methods and refined to *R*₁ = 0.066, *R*₂ = 0.087 on the basis of 5101 independent reflections. Data were measured with use of Mo K α radiation and a Syntex P2₁ diffractometer. There are strong π ··· π interactions between the cation molecules, and the structure is stabilized by an extensive hydrogen-bonding network. There is no structural or spectral evidence for covalent interaction between the Pt atoms and the dye molecules. This result is discussed in light of the anticancer properties of the compound.

Introduction

Although a variety of Pt complexes have been shown to possess clinical anticancer properties, none of these compounds are selectively taken up by tumors.¹ There is great interest in finding

active Pt compounds that are targeted to tumors. Chen et al. have recently shown that the cationic dye Rhodamine 123 (RH(123)) is selectively retained in the mitochondria of carcinoma cells compared to normal cells in tissue culture.² The chemical structure of the RH(123) cation is shown in Figure 1. In an attempt to form a complex of RH(123) and Pt, the reaction of

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(1) Owens, S. E.; et al. *Cancer Chemother. Pharmacol.* **1985**, *14*, 253–257.

(2) Summerhayes, I. C.; Lampidis, T. J.; Bernal, S. D.; Nadakavukaren, J. J.; Nadakavukren, K. K.; Shepard, E. L.; Chen, L. B. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 5292–5296.