

A New Tetrathiafulvalenium Complex with Copper Chloride: Electrical and Magnetic Properties

Motomichi Inoue* and Michiko B. Inoue

CIPM, University of Sonora, AP 130, Hermosillo, Sonora, Mexico

High electrical powder conductivity (14 S cm^{-1} at 300 K) and unusual temperature dependence were observed for a new tetrathiafulvalene (TTF) compound, $[(\text{TTF})_2]^+\text{Cu}^+\text{Cl}_2$, which was prepared by oxidation of TTF with copper(II) chloride; the compound was characterized by e.s.r. and i.r. spectra as well as magnetic susceptibility.

Some 1,4,5,8-tetrathiafulvalene (TTF) salts have been found to exhibit high electrical conductivity which shows metal-like temperature dependence.¹ These 'molecular metals' were prepared by oxidation of TTF with oxidants such as Cl_2 , I_2 , and 7,7,8,8-tetracyanoquinodimethane (TCNQ) or by electrochemical oxidation.¹ One of the features of the molecular metals is that the constituent molecules are in a mixed-valence (or intermediate oxidation) state; the formation of molecular metals requires appropriate conditions for oxidizing TTF. Extensive efforts have been made in the search for new ways to prepare a variety of molecular metals. This paper reports a new type of highly conducting TTF compound that can be prepared by using copper(II) chloride as an oxidant.

$(\text{TTF})_2\text{CuCl}_2$ was obtained as a dark purple powder by adding a methanol solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 mmol) to a methanol solution of TTF (0.22 mmol) under a nitrogen atmosphere.

The compressed pellets exhibited high electrical conductivity (14 S cm^{-1} at 300 K), which showed unusual temperature dependence as shown in Figure 1. It is noteworthy that the powder conductivity is temperature-independent above ca. 250 K: the intrinsic conductivity may be metallic. Below ca. 160 K, the conductivity decreased rapidly with decreasing temperature: the material is semiconducting at lower temperatures, although the semilogarithmic plot of the conductivity vs. reciprocal temperature does not yield a straight line. This indicates the occurrence of a phase transition probably from a metallic state to a semiconducting state. This phase transition is reflected in the temperature dependence of the magnetic

susceptibility (Figure 1): temperature-independent paramagnetism ($3.3 \times 10^{-4} \text{ e.m.u. mol}^{-1}$ per compound formula), which is characteristic of extensively delocalized spins, is displayed above ca. 220 K, and an abrupt change from

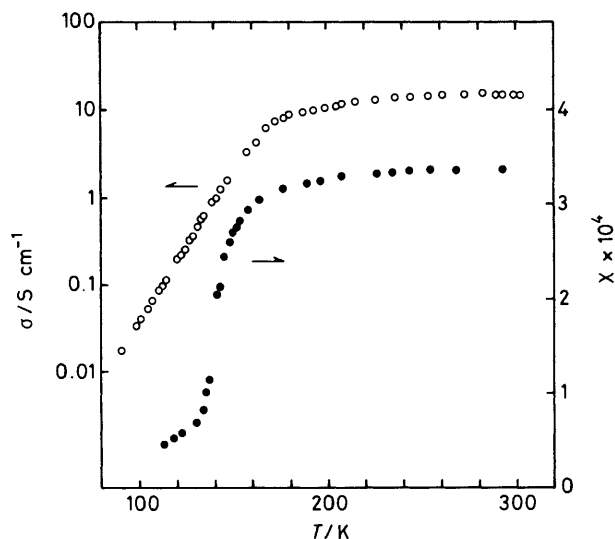


Figure 1. Temperature dependence of electrical powder conductivity, σ , and magnetic susceptibility, χ , (per compound formula in e.m.u. mol^{-1}) of $(\text{TTF})_2\text{CuCl}_2$.

paramagnetism to diamagnetism takes place between 130 and 160 K.

The e.s.r. spectrum displayed a single symmetric signal with a g value of 2.0063, which is nearly equal to the value (2.00838) of TTF^+ in solution.² The paramagnetism arises from the organic radicals; the copper atoms are in the diamagnetic Cu^{I} state. The i.r. spectrum exhibited a very broad band extending from 1000 to 4000 cm^{-1} . Below the band edge, two peaks assignable to the b_{1u} -16 and b_{2u} -25 modes³ of TTF appeared at 805 and 816 cm^{-1} . These wavenumbers are intermediate between those of TTF^0 and TTF^+ : the b_{1u} -16 mode appears at 781 and 836 cm^{-1} for TTF^0 and TTF^+ , respectively, and the b_{2u} -25 mode at 794 and 825 cm^{-1} for TTF^0 and TTF^+ , respectively.³ This suggests a fractional-charge occupation of TTF. The formula can be written as $[(\text{TTF})_2]^+\text{Cu}^+\text{Cl}_2$ in which two TTF constituents share +1 charge.

When copper(II) bromide was used as an oxidant in place of the chloride, $(\text{TTF})_{5/3}\text{CuBr}_2$ was obtained under the same reaction conditions as mentioned above. The powder conductivity, σ (1.5 S cm^{-1} at 297 K) followed $\sigma = \sigma_\infty \exp(-E/kT)$ with $E = 0.05$ eV between 100 and 300 K. The magnetic susceptibility per compound formula was 1.3×10^{-4} and 1.1×10^{-4} e.m.u. mol^{-1} at 297 and 114 K, respectively. The e.s.r. spectrum showed a single symmetric signal with $g = 2.0065$: TTF radicals are the paramagnetic species involved. A broad i.r. band assignable to b_{1u} -16 and/or b_{2u} -25 was observed at 825 cm^{-1} .

The formation of the complexes accompanies the partial oxidation of TTF, shown in equation (1). Siedle, *et al.*⁴ have



reported that Cu^{2+} ions can oxidize TTF^0 to TTF^+ or TTF^{2+} ; the resulting salts were poorly conducting (10^{-2} — 10^{-5} S cm^{-1} at room temperature). The present study, however, demonstrates that under appropriate conditions, Cu^{II} compounds can function as excellent oxidants to form mixed-valence TTF compounds that are highly electroconductive. This together with our previous studies⁵ of Cu -TCNQ complexes shows that the use of copper compounds as donors or acceptors may afford a versatile way to design various types of highly conducting materials.

This research was supported by grants from the Secretaría de Educación Pública, Mexico.

Received, 29th April 1985; Com. 569

References

- 1 Proceedings of the International Conference on Low-Dimensional Conductors, parts B, E, and F, published in *Mol. Cryst. Liq. Cryst.*, 1982, **79**, **85**, and **86**.
- 2 F. Wudl, G. H. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1970, 1453.
- 3 For the numbering of the vibrational modes of TTF, see: R. Bozio, I. Zanon, A. Girlando, and C. Pecile, *J. Chem. Phys.*, 1979, **71**, 2282.
- 4 A. R. Siedle, G. Z. Candela, T. F. Finnegan, R. P. Van Duyne, T. Cape, G. F. Kokoszka, P. M. Woyciejes, and J. A. Hashmall, *Inorg. Chem.*, 1981, **20**, 2635.
- 5 M. Inoue and M. B. Inoue, *J. Chem. Soc., Chem. Commun.*, 1984, 790; M. Inoue and M. B. Inoue, *J. Chem. Soc., Faraday Trans. 2*, 1985, 539.