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Highly-conducting neutral copper complexes substituted with two tetrathiafulvalenyldithiolato groups

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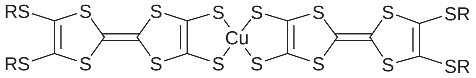
The neutral bis(dialkylthiotetrathiafulvalenyldithiolato)copper complexes, $Cu(R_2C_6S_8)_2$ (R = Me **1a**, Et **1b**, $R_2 = -CH_2CH_2-$ **1c**) were synthesized by the reaction of bis(tetramethylammonium or tetraethylammonium) bis(dialkylthiotetrathiafulvalenyldithiolato)zincate complexes with $CuCl_2$ in DMF, followed by oxidation with iodine. The room-temperature electrical conductivities were 7.8×10^{-2}, 5.0×10^{-4} and 3.7 S cm^{-1} for compressed pellets of **1a**, **1b** and **1c**, respectively. Magnetic susceptibility measurements showed that the remaining spin on the copper atoms is very small for these complexes as a result of large intramolecular electron transfer from Cu^{II} atom to the tetrathiafulvalenyl radical cation ligands.

Much effort continues to be directed toward the synthesis of new organic complexes with localized d electrons on the metal atom and conducting π electrons on the ligand.[1] So far, oxidatively doped copper(II)[2–8] and cobalt(II)[9] metallophthalocyanines are well-known typical π–d cooperative systems. These systems form a one-dimensional array of paramagnetic local moments in the conducting framework of the organic phthalocyanine ligands. Furthermore, the copper salt of 2,5-dimethyl-*N*,*N*′-dicyano-*p*-benzoquinonediimine[10] and the charge-transfer complexes of several tetrathiafulvalene derivatives with associated magnetic metal ions[11–14] provide two- or three-dimensional π–d cooperative systems. Our interest concerns the synthesis of a new type of organic complexes with magnetic metal ions incorporated through covalent bonds into a two- or three-dimensional π conducting network, since a strong π–d interaction can be expected in their molecular crystals and unique electrical conducting and magnetic properties might result. Here, we report the synthesis of neutral copper complexes substituted with bis(dimethylthio-, diethylthio- and ethylenedithio-tetrathiafulvalenyldithiolato) ligands (**1a**, **1b** and **1c**), and their electrical conducting and magnetic properties.

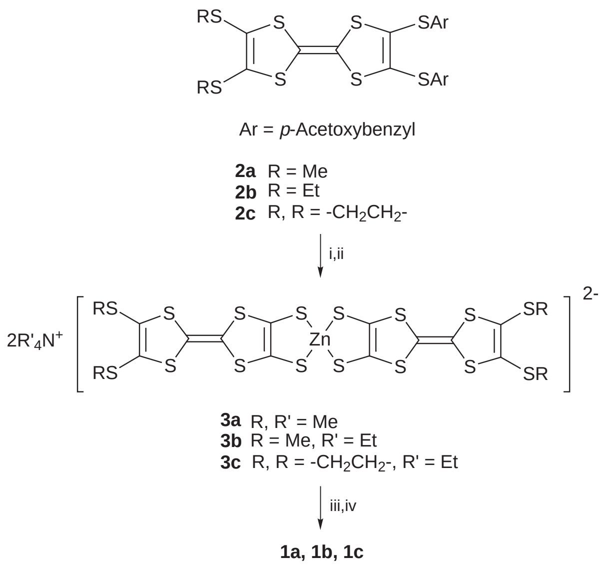


1a R = Me
1b R = Et
1c R,R = $-CH_2CH_2-$

Experimental

Synthesis of neutral bis(dialkylthiotetrathiafulvalenyldithiolato)copper complexes 1

The synthetic procedure is shown in Scheme 1. Sodium (9.0 mmol) was added to bis(*p*-acetoxybenzylthio)bis(dialkylthio)tetrathiafulvalene **2**[15,16] (0.30 mmol) in MeOH (15 ml) at room temperature under argon, and the reaction mixture was stirred for 30 min, followed by the addition of Me_4NBr or Et_4NBr (0.60 mmol) and $ZnCl_2$ (0.30 mmol) and further stirring for 2 h. The resultant precipitate, bis(tetramethylammonium) or bis(tetraethylammonium) bis(dialkylthiotetrathiafulvalenyldithiolato)zincate **3**[17] was filtered off, washed with MeOH and finally dried *in vacuo*. To $CuCl_2$ (0.12 mmol) in DMF (10 ml) was added **3** (0.10 mmol) in DMF (10 ml) at −40 °C under argon, and stirring was continued overnight at room temperature. After removing the solvent a green solid was collected, washed with MeOH and dried *in vacuo*. Reaction of this green solid with an excess of iodine in DMF (10 ml) was carried out at −40 °C under argon, followed by solvent removal, washing with MeOH and drying *in vacuo* to give **1**.



Scheme 1 *Reagents and conditions*: i NaOMe, MeOH, room temperature, 30 min; ii R'_4NBr (R′ = Me, Et), $ZnCl_2$, room temperature, 2 h; iii $CuCl_2$, DMF, −40 °C, 12 h; iv I_2, DMF, −40 °C, 12 h.

Bis(dimethylthiotetrathiafulvalenyldithiolato)copper **1a**:[18] 45% yield; green solid (mp > 300 °C); Anal. Calc. for $C_{16}H_{12}S_{16}Cu$: C, 24.61; H, 1.55. Found: C, 24.48; H, 1.78%.

Bis(diethylthiotetrathiafulvalenyldithiolato)copper **1b**: 96% yield; dark green powder [mp ≈150 °C (decomp.)]; Anal. Calc. for $C_{20}H_{20}S_{16}Cu$: C, 28.70; H, 2.41. Found: C, 28.77; H, 2.65%. Bis(ethylenedithiotetrathiafulvalenyldithiolato)copper **1c**: 96% yield; dark green powder (mp > 300 °C); Anal. Calc. for $C_{16}H_8S_{16}Cu$: C, 24.74; H, 1.04. Found: C, 24.48; H, 1.28%.

Electrical conductivities

Electrical conductivities were measured on compressed pellets by using a four-probe method at various temperatures between 5 and 300 K; electrode contacts were made using gold paste.

Magnetic susceptibilities

Magnetic susceptibilities (χ_{obs}) were measured in the temperature range 5–300 K at an applied field of 1 kOe using a SQUID magnetometer (MPMS XL, Quantum Design). The paramagnetic susceptibility was obtained by subtracting the diamagnetic contributions, calculated using Pascal's constants, from χ_{obs}.

EPR spectra

The EPR spectra were recorded by using a JEOL 1X spectrometer with Mn^{2+}/MgO used as calibrant.

MO calculation method

MO calculations were performed with the ZINDO program,[19] which allows for the treatment of transition-metal complexes and the inclusion of extensive configuration interaction.

Results and Discussion

MO calculations

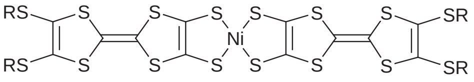
The molecular structures of **1a**, **1b** and **1c** are unknown since no single crystals suitable for the X-ray structure analysis could be obtained. Furthermore, there are no reports on the crystal structures of any neutral bis(dithiolato)copper complexes. Nevertheless, a number of mono- and bis-anionic salts of bis(dithiolato)copper complexes have been crystallographically characterized and the geometry around the copper atom shown to be variable. The tetra-*n*-butylammonium salt of bis(maleonitriledithiolato)cuprate(III)[20] and the bis(tetra-*n*-butylammonium) salt[21,22] of the corresponding cuprate(II) complex have almost planar geometry around the copper atom. On the other hand, a relatively large distortion from planarity (41.1–57.3°) was seen for the bis(tetramethylammonium)[23] and bis(Methylene Blue) salts[24] of bis(maleonitriledithiolato)cuprate(II) and for the bis(*N*-ethylpyridinium) salt of the bis(4,5-dimercapto-1,3-dithiole-2-thionato)cuprate(II) complex.[25] ZINDO MO calculations of a parent system of **1**, a neutral bis(tetrathiafulvalenyldithiolato)copper complex (**1′**) were performed on two extreme cases in which the geometries around the copper atom are planar and distorted by 57.3° from planarity. The formal charges on the copper atom obtained by Mulliken population analyses were 1.552 and 1.385 for the planar and 57.3°-distorted geometries, respectively. For comparison, similar calculations were also performed on the planar bis(maleonitriledithiolato)-copper(II) and -copper(III) complexes, and the formal charges on the copper atom were 1.442 and 1.539 respectively. Obviously, the copper atom in **1′** with planar geometry is close to the Cu^{III} state, and with increasing distortion from planar geometry the copper atom gradually approaches the Cu^{II} state. This implies that distortion from planar geometry decreases the electron transfer from Cu^{II} to the TTF radical cation ligands because of a decreased d–π interaction. As is mentioned later, the spin on the copper atoms is almost zero for **1a**–**1c**, where the copper atom is in the Cu^{III} state. From this result it is probable that the geometry around the copper is near planar for all the complexes.

Table 1 Electrical conductivities for **1a**, **1b** and **1c** at room temperature

	σ_{rt}/S cm^{-1}	E_a/eV
1a	7.8×10^{-2}	
1b	5.0×10^{-4}	
1c	3.7	0.05

Electrical conducting properties of 1a, 1b and 1c

Table 1 shows the electrical conductivities (σ) at room temperature (σ_{rt}) and activation energies (E_a) for compressed pellets of the three copper complexes. The σ_{rt} values of **1a**, **1b** and **1c** are 7.8×10^{-2}, 5.0×10^{-4} and 3.7 S cm^{-1}, respectively, which are comparable to those of neutral bis(tetrathiafulvalenyldithiolato)nickel complexes (**4**) (10^{-4}–10^{-1} S cm^{-1})[26] and bis(benzene-1,2-dithiolato)aurate (1×10^{-3} S cm^{-1}).[27] It is notable that the σ_{rt} value of **1c** is remarkably high. The temperature dependence of the σ value was investigated in the temperature range 5–300 K, and semiconducting behavior with a gradual decrease in σ with lowering temperature was observed. The σ *vs.* T plot obeyed the relation $\sigma = A\exp(E_a/kT)$, with E_a equal to 0.05 eV from the slope of the ln σ *vs.* T^{-1} plot, as shown in Fig. 1. This value is very low, suggesting the possibility of metal-like behavior in a σ *vs.* T plot for, as yet, unavailable single crystals. The σ_{rt} values are strongly dependent on the kinds of substituents on the tetrathiafulavalenyl rings. Thus, the smaller the bulkiness of the alkylthio group, the higher is the σ_{rt} value. A similar tendency was also observed in **4**;[26] σ_{rt} values were 10^{-1}, 10^{-1} and 10^{-4} S cm^{-1} on compressed pellets for the methylthio- (**4a**), ethylthio- (**4b**) and *n*-butylthio-substituted derivatives (**4c**), respectively. A much larger σ_{rt} value might be obtained for the ethylenedithio-substituted derivative, unfortunately not synthesized in the study, on the basis of the present results. These results suggest that the alkylthio substituent exerts an important influence on the stacking mode between the tetrathiafulvalenyl moieties in **1** and **4**, which is responsible for the magnitude of electrical conductivity. Information on the stacking modes can be only obtained from the crystal structure of **4b**. The geometry around the nickel atom is square-planar and the eight sulfur atoms of one diethylthio-substituted tetrathiafulvalenyldithiolato ligand are essentially coplanar. Owing to the ethylthio groups projecting out of the molecular plane, the molecules can not completely overlap with each other, but are stacked with a interplanar distance of *ca.* 3.4 Å in a slightly slipped manner. Accordingly, the intermolecular nickel–nickel distance is large (5.17 Å). Such a partial stacking mode between the tetrathiafulvalenyl moieties is considered as one of the reasons for the only moderate electrical conductivity. Considering this fact in combination with the higher electrical conductivity for **1c**, it is expected that much more tight stacking occurs between the tetrathiafulvalenyl moieties as a result of sterically less hindered ethylenedithio groups. On the other hand, **1a** and **1b** might adopt a similar stacking to that of **4b**. However, this conclusion must await X-ray structure analysis on single crystals of **1a**, **1b** and **1c**, which are now being attempted to be prepared. In addition, the amount of positive charge residing on each tetrathiafulvalenyl moiety is



4a R = Me
4b R = Et
4c R = Bu^n

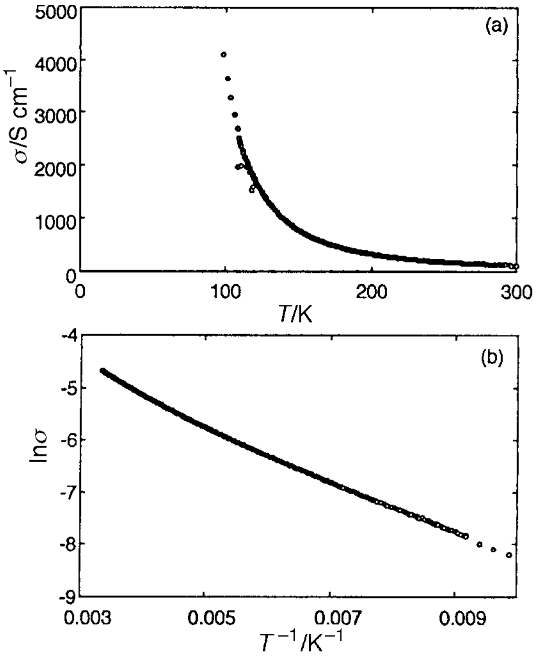


Fig. 1 Temperature dependence of electrical conductivity (σ) in the temperature range 5–300 K: (a) σ *vs.* T and (b) ln σ *vs.* T^{-1} plots.

responsible for the comparatively high electrical conductivities. Thus, if copper is in a divalent oxidation state (Cu^{II}) (Scheme 2), a 1+ charge must be placed on each tetrathiafulvalenyl moiety in order to maintain charge neutrality for the complexes. In this case it is difficult to produce a high electrical conductivity since a mixed-valence state can not be achieved in the tetrathiafulvalenyl stacks. In the other extreme, trivalent copper (Cu^{III}) induces a 0.5+ charge into each of the tetrathiafulvalenyl moieties, thereby leading to a mixed-valence state for the tetrathiafulvalenyl stacks. Of course, intermediate oxidation states of copper also enable production of a high electrical conductivity. As discussed below, the copper atom is virtually in the trivalent oxidation state leading to the production of a high electrical conductivity for all the complexes.

$$(TTF^{0})Cu^{(III)-}(TTF^{\bullet+}) \longleftrightarrow (TTF^{\bullet+})Cu^{(II)2-}(TTF^{\bullet+}) \longleftrightarrow (TTF^{\bullet+})Cu^{(III)-}(TTF^{0})$$

Scheme 2.

Magnetic properties of 1a, 1b and 1c

The temperature dependence of the paramagnetic susceptibility (χ_p) was investigated in the temperature range 5–300 K for **1a**, **1b** and **1c** and results are shown in Fig. 2. Fig. 3 depicts the temperature dependence of $\chi_p T$ where a linear relationship is observed in the higher temperature region, suggesting the presence of a temperature-independent susceptibility (denoted χ_π). An almost temperature-independent susceptibility in the low temperature region of the Bonner–Fisher curve is obtained as a result of strong antiferromagnetically interacting spins of tetrathiafulvalenyl radical cations in the present complexes. $\chi_{Cu}(T)$ ($=\chi_p-\chi_\pi$) is the contribution from the localized spin on the copper atom, and obeys the Curie–Weiss law. Accordingly, the observed temperature dependence of χ_p can be expressed by eqn. (1)

$$\chi_p(T)=\chi_{Cu}(T)+\chi_\pi=C/(T-\theta)+\chi_\pi \qquad (1)$$

where C is the Curie constant and θ the Weiss temperature. Similar χ_p *vs.* T behavior has previously been seen in (phthalocyaninato)copper iodide [Cu(pc)I][8] and (phthalocyaninato)-cobalt hexafluoroarsenate [Co(pc)AsF$_6$],[9] where the con-

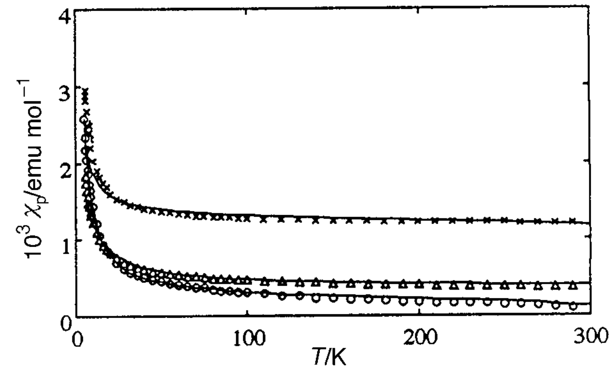


Fig. 2 Temperature dependence of paramagnetic susceptibilities (χ_p) obtained for **1a** (×), **1b** (○) and **1c** (△). The solid lines are reproduced using the C, θ and χ_π values listed in Table 2.

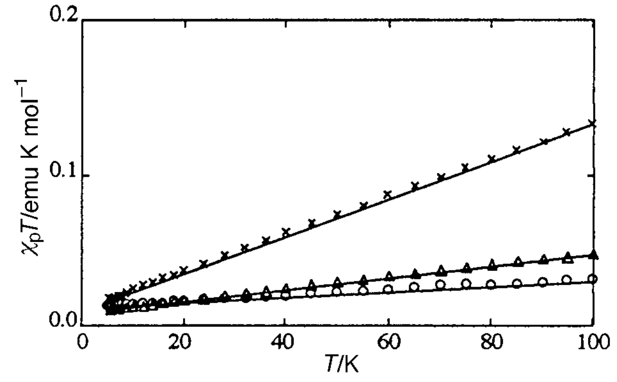


Fig. 3 Temperature dependence of $\chi_p T$ for **1a** (×), **1b** (○) and **1c** (△). The solid lines are reproduced using the C, θ and χ_π values listed in Table 2.

ducting π electrons and the localized d spins coexist and interact with each other. By fitting C, θ and χ_π values in the above equation, the observed χ_p *vs.* T behavior was well reproduced for each complex and values are summarized in Table 2. The C values are 1.0×10^{-3}, 1.0×10^{-2} and 1.2×10^{-2} emu K mol^{-1} for **1a**, **1b** and **1c**, respectively, which correspond to 0.24, 2.7 and 3.2% of that calculated by the equation of $C=N\mu_B{}^2g^2S(S+1)/3k_B$, where N is Avogadro's number, μ_B the Bohr magneton, k_B is the Boltzmann constant, S the spin magnetic quantum number, and g an average g factor of the Cu^{II} spin, respectively. As can be readily seen from the very small C values, spin on copper is scarcely present, and the copper atom is essentially in the Cu^{III} state. However, a very small amount of spin still remains on the copper atom, and the interaction between the neighboring spins is weakly-antiferromagnetic, as shown by the small value and negative sign in θ. The χ_π values are 9.1×10^{-4}, 1.9×10^{-4} and 3.6×10^{-4} emu mol^{-1} for **1a**, **1b** and **1c**, respectively, and comparable to those (1.9×10^{-4} and 4.3×10^{-4} emu mol^{-1}) for Cu(pc)I[8] and Co(pc)AsF$_6$,[9] respectively.

EPR spectra

All of the three copper compounds showed only one broad signal in their solid EPR spectra. The g values were 2.0075 for **1a**, 2.0089 for **1b** and 2.0110 for **1c**. By contrast, for both

Table 2 The C, θ and χ_π values for **1a**, **1b** and **1c**

	C/emu K mol^{-1}	θ/K	χ_π/emu mol^{-1}
1a	1.0×10^{-3}	~0	9.1×10^{-4}
1b	1.0×10^{-2}	−1.2	1.9×10^{-4}
1c	1.2×10^{-2}	−4.2	3.6×10^{-4}

planar and non-planar bis(dithiolato)copper(II) complexes already characterized, two different signals were observed at $g_{\parallel} \approx 2.09$ and $g_{\perp} \approx 2.02$ in the solid state. A most probable cause for the present behaviour is the exchange of the Cu^{II} spin with other spins, the TTF radical cation in this case, giving rise to coalescence of two different signals due to the Cu^{II} spin state. Nevertheless, the magnetic measurement results above showed that the spin on the copper atoms is very small (0.24 for **1a**, 2.7 for **1b** and 3.2% for **1c**) because of almost complete electron transfer from Cu^{II} to the TTF moieties. When strong exchange occurs between the Cu^{II} spin and the TTF radical cation, the observed g value can be determined by eqn. (2)

$$g = \chi_{Cu} g_{Cu}/\chi_{total} + \chi_{\pi} g_{\pi}/\chi_{total} \qquad (2)$$
$$\chi_{total} = \chi_{Cu} + \chi_{\pi}$$

where g_{Cu} and g_{π}, and χ_{Cu} and χ_{π} are the g values and local magnetic susceptibilities contributed from the Cu^{II} spin and the TTF radical cation, respectively, and χ_{total} the total magnetic susceptibility. However, since in the present case the spin on the copper atom is very small, only a very small increase from the g value (2.0072) of the radical cation salt of tetramethylthio-substituted TTF is expected. Of course, the degree of shifting (Δg) is strongly dependent on the amount of spin on the copper atom. The Δg values are 0.0003, 0.0017 and 0.0038 for **1a**, **1b** and **1c**, respectively, which are consistent with an increase in the spin on the copper atom along this series.

Conclusions

Our initial interest in **1** lies in it containing both π radical cations (TTF ligands) and a d spin on the Cu^{II} moieties, which are located separately from each other. A two- or three-dimensional array of **1** could provide a unique organic solid system involving both conducting π electrons and localized d spins in interaction with each other, and novel electrical conducting and magnetic properties might result. However, in contrast to this expectation a large degree of intramolecular electron transfer from Cu^{II} to the TTF radical cation ligands occurs, giving rise to almost no spin on the resultant Cu^{III} atom. On the other hand, the one electron transferred from the Cu^{II} atom can be equally accepted by the two TTF radical cation ligands. Consequently, a +0.5 radical cation resides on each TTF ligand, so that a mixed valence state can be achieved, if the TTF ligands are effectively stacked. In fact, the present neutral copper complexes exhibited comparatively high electrical conductivities without any doping. Several organic metal complex-based intrinsic conductors are known so far. Their single crystal σ_{rt} values lie in the range 10^{-4}–10^{-1} S cm^{-1}. In comparison the higher σ_{rt} value of **1c** measured on a compressed pellet is of significance.

Other magnetic metal ions than Cu^{II}, *e.g.* Cr^{III} ($S = 3/2$), Mn^{II} ($S = 5/2$ or $1/2$), Co^{II} ($S = 1/2$) and Fe^{III} ($S = 5/2$ or $1/2$), can also be used in the preparation of the similar neutral complexes to **1**. From these new complexes different electrical conducting and magnetic properties from those of **1** might be observed. We are presently preparating the neutral cobalt and iron complexes.

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