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Copper and Gold Metallotetrathiaethylenes

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Oxidation of tetrathiafulvalene (TTF) with $Cu(BF_4)_2$ in acetonitrile yielded $(TTF)(BF_4)_2$, a salt of the TTF dication. In acetonitrile, $(TTF)CuCl_4$ was formed from $CuCl_2\cdot2H_2O$. In ethanol, $(TTF)_3(CuCl_2)_5$ was obtained; it was converted, by recrystallization from acetonitrile, to $(TTF)_2CuCl_4$. From $CuBr_2$ and TTF in acetonitrile, $(TTF)CuBr_3$ was obtained, but in ethanol $(TTF)_3(CuBr_2)_5$ was produced. Oxidation of TTF with $HAuCl_4\cdot3H_2O$ in acetonitrile or ethanol yielded $(TTF)AuCl_2$ and $(TTF)(AuCl_4)_2$, respectively. These new metallotetrathiaethylenes were characterized by electronic, vibrational, EPR, and X-ray photoelectron spectroscopy and by measurement of the magnetic susceptibilities and electrical conductivity. Resonance Raman spectroscopy (RRS) proved especially valuable. The ν_3 mode, involving primarily stretching of the central $C=C$ bond in TTF, shifts from 1512 cm^{-1} in TTF^0 to 1416 and 1308 cm^{-1} in TTF$^+\cdot$ and TTF^{2+}, respectively. These large shifts are useful in assigning the oxidation state(s) of the TTF moiety in metallotetrathiaethylenes. For example, bands at 1418 and 1298 cm^{-1} in $(TTF)_3(CuCl_2)_5$ indicate that is is a mixed-valence material formulated as $(TTF^+\cdot)(TTF^{2+})_2(CuCl_2^-)_5$.

Introduction

The structural and electronic properties of tetrathiafulvalene (TTF) (**1**) are considered to be important determinants of electrical-transport properties in crystals of donor–acceptor complexes such as TTF–TCNQ.[2-5] While materials from **1** and a very wide variety of organic acceptor molecules have been prepared and studied, less information is available concerning metallotetrathiaethylenes, materials formed from TTF or related thiacarbons, and inorganic or organometallic compounds.[6,7]

Transition-metal dithiolene complexes of TTF of the type $[(CF_3)_2C_2S_2]_2M(TTF)$ (M = Ni, Pt),[8] $[(C_2H_2S_2)_2Ni](TTF)_2$[9] and $(TTF)_2[(CN)_2C_2S_2]M$ (M = Cu, Co, Ni, Pt) have been described, and spin-Peirls transitions have been observed in 1:1 adducts of TTF and $[(CF_3)_2C_2S_2]_2M$ (M = Cu, Au).[10-12] More recently, novel transition-metal complexes of tetrathianaphthalene (TTN) have been reported.[14-18] The sulfur–sulfur bond in this ligand is evidently ruptured so that the thiacarbon behaves as a highly reactive disulfide in which extensive charge delocalization is possible. We have recently described several TTF chlorocuprates[19] and the trichloromercurate salt of the TTF cation radical.[20] As part of a systematic study of inorganic compounds containing TTF, we have no prepared a series of copper and gold derivatives. This paper reports the synthesis and characterization of these materials.

Results

The Tetrathiafulvalenium Dication. It is appropriate to discuss the TTF dication at this point since this ion occurs in compounds to be described later and because the synthesis illustrates the effect of solvent on the chemistry of the TTF–Cu^{2+} system. A previous report of TTF^{2+} disclosed the preparation of the dichloride from **1** and excess chlorine.[21]

Addition of an ethanol solution of **1** to excess $Cu(BF_4)_2$ in the same solvent produced $(TTF)_3(BF_4)_2$ (**2**), whose X-ray powder pattern matched that of the product obtained by using either $AgBF_4$ or Ph_3CBF_4[22] as the oxidant. When the same reaction was carried out in acetonitrile, small off-white crystals of $TTF(BF_4)_2$ (**3**) were obtained. Since the fluoborate ion can have only a unit negative charge, **3** is clearly a salt of TTF^{2+}.

Table I. Electronic Spectra and Conductivity Data

compd	λ_{max}, nm^a	σ, $(\Omega$ cm$)^{-1}$
$(TTF)(BF_4)_2$ (**3**)	540, 380	
$(TTF)CuCl_4$ (**4**)	445	5×10^{-4}
$(TTF)_3(CuCl_2)_5$ (**5**)	780, 650 (sh), 445, 415, 265	10^{-5}
$(TTF)_2CuCl_4$ (**6**)	880, 500, 380	5×10^{-5}
$(TTF)_3(CuBr_2)_5$ (**7**)	950, 900 (sh), 460, 345, 240	2×10^{-3}
$(TTF)(CuBr_3)_{0.4}$ (**8**)	1600, 975, 925, 540, 390 (sh), 330	4×10^{-2}
$(TTF)CuBr_3$ (**9**)	443	7×10^{-4}
$(TTF)_3[Cu(NO_3)_2]$ (**10**)	680 (sh), 530, 365, 260	5×10^{-2}
$(TTF)_2NO_3$ (**11**)		5×10^{-2}
$(TTF)AuCl_2$ (**12**)	850, 550, 410, 225	3×10^{-3}
$(TTF)(AuCl_4)_2$ (**13**)	530, 375	3×10^{-4}
$(TTF)_3(BF_4)_2$	840, 535, 375, 335, 215	

In a potassium bromide matrix, **3** exhibited λ_{max} at 380 and 540 nm (Table I). On exposure to the atmosphere, the salt slowly developed a brown color. Solutions in acetonitrile were

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Table II. Infrared Absorption Maxima (cm⁻¹)

TTF (1)	3050 (w), 1520 (w), 1250 (m), 1035 (w), 1020 (w), 865 (s), 730 (m), 630 (s), 435 (m)
(TTF)₃(BF4)₂ (2)	3080 (w), 1510 (w), 1355 (s), 1120 (s), 1040 (br, s), 820 (m), 795 (m), 745 (s), 740 (s), 695 (m), 670 (s), 520 (m), 490 (s), 460 (s), 435 (m)
(TTF)(BF4)₂ (3)	3090 (m), 1440 (s), 1375 (w), 1285 (w), 1270 (w), 1050 (br, vs), 870 (s), 755 (s), 745 (s), 520 (s)
(TTF)CuCl₄ (4)	3060 (w), 3030 (w), 1425 (s), 1405 (w), 1340 (m), 1250 (s), 1070 (w), 955 (m), 905 (m), 865 (m), 780 (s), 760 (s), 735 (s), 395 (m)
(TTF)₃(CuCl₂)₅ (5)	3015 (w), 1500 (w), 1460 (w), 1430 (s), 1410 (w), 1345 (s), 1250 (s), 1230 (w), 1070 (m), 955 (m), 860 (m), 820 (w), 770 (w), 750 (s), 730 (s), 700 (m), 485 (m), 395 (m)
(TTF)₂CuCl₄ (6)	3010 (w), 1495 (m), 1380 (br, s), 1255 (w), 1230 (m), 1070 (m), 950 (w), 880 (w), 835 (s), 820 (s), 750 (s), 740 (s), 700 (s), 695 (sh), 480 (s), 460 (m)
(TTF)₃(CuBr₂)₅ (7)	3040 (m), 1430 (s), 1410 (w), 1345 (s), 1335 (sh), 1250 (s), 1230 (w), 1070 (w), 950 (m), 890 (w), 860 (m), 770 (m), 740 (s), 725 (s), 485 (m), 465 (w), 390 (m)
(TTF)(CuBr₃)₀.₄ (8)	3010 (w), 1500 (w), 1430 (w), 1405 (s), 1375 (m), 1395 (s), 1230 (s), 1070 (s), 835 (m), 825 (s), 820 (s), 745 (sh), 740 (s), 695 (s), 690 (m), 640 (m), 480 (s), 465 (m), 455 (w), 355 (w)
(TTF)CuBr₃ (9)	3015 (w), 1430 (s), 1405 (w), 1260 (m), 1250 (s), 1070 (w), 1065 (w), 950 (w), 935 (w), 840 (m), 785 (s), 770 (s), 740 (s), 725 (s), 505 (w), 495 (w), 460 (w), 450 (w), 385 (w)
(TTF)₃Cu(NO₃)₂ (10)	1350 (s), 1240 (s), 1250 (w), 1235 (w), 1120 (m), 830 (m), 815 (m), 735 (m), 690 (m), 610 (w), 480 (s)
(TTF)₂NO₃ (11)	1360 (s), 1250 (s), 1085 (m), 825 (m), 815 (w), 740 (m), 480 (s), 460 (m)
(TTF)AuCl₂ (12)	3000 (w), 1495 (m), 1465 (m), 1455 (m), 1365 (s), 1355 (s), 1235 (s), 1205 (w), 1080 (w), 1065 (m), 1035 (w), 855 (w), 830 (s), 785 (m), 750 (s), 705 (s), 485 (s), 460 (m), 355 (s)
(TTF)(AuCl₄)₂ (13)	2985 (w), 1445 (m), 1270 (m), 1085 (w), 1070 (w), 980 (m), 970 (m), 870 (w), 735 (s), 525 (w), 345 (s)

Table III. Frequencies and Frequency Changes for the A_g Modes of TTF⁰, TTF⁺, and TTF²⁺ [a]

A_g mode	TTF⁰	TTF⁺	TTF²⁺	(TTF⁰)-(TTF⁺)	(TTF⁺)-(TTF²⁺)	(TTF⁰)-(TTF²⁺)
ν_2	(1560)	1510	1442	-38	-68	-106
ν_2	1548	1481		-67	-39	
ν_3	1512	1416	1308	-96	-108	-204
ν_4	1087	1088	1079	+1	-9	-8
ν_5	796	758	784	-38	+26	-12
ν_6	468	506	542	+38	+36	+74
ν_6			527		+21	+59
ν_7	250	264	270	+14	+6	+20

[a] All frequencies are given in cm⁻¹ and were obtained with 4579- or 5145-Å excitation.

extremely sensitive to moisture, and, on addition of water, only the characteristic electronic spectrum of the TTF cation radical was observed. Following the analysis of the Raman spectrum of solid TTF,[23] the band at 1440 cm⁻¹ in the infrared spectrum of **3** (Table II) may be assigned to C=C vibrations in the five-membered ring, the 1285- and 1270-cm⁻¹ bands to C–H group vibrations, the 755–745-cm⁻¹ bands to skeletal C–S vibrations. Strong Raman bands at 1002 and 763 cm⁻¹ are attributable to BF₄⁻.

Table III compares the Raman spectra of TTF⁰, TTF⁺· (an average value from 11 compounds), and TTF²⁺(BF₄)₂. The ν_3 mode in TTF²⁺ occurs at 1323 cm⁻¹. Of the seven A_g normal modes in **1** the ν_3 mode, which is predominantly the central C=C stretch, undergoes the largest frequency shift on oxidation. These large shifts, approximately 100 cm⁻¹ per unit charge, combined with the fact that the scattering is resonance enhanced, make resonance Raman spectrscopy a powerful tool with which to study TTF derivatives.

Reduction of TTF²⁺ by sodium borodeuteride in acetonitrile proceeded by both electron an deuteride transfer. The former process produced **1** while deuteride addition to C(2,2′) afforded 2,2′-dideuteriobis(2,2′-dithiolyl).[25] ¹H NMR analysis of the

reaction mixture indicated a 3:2 ratio of **1** and bis(dithiolyl). A control experiment showed that no reaction occurred between **1** and NaBD₄ under the same reaction conditions. More recently, hydride transfer from NaBH₃CN to p-phenylene-bis(1,3-benzodithiolium) fluoborate has been reported.[26] The solvent dependence on the oxidation of TTF by Cu²⁺ arises from the more effective solvation of Cu(I) by acetonitrile[27,28] than by ethanol. Thus, copper(II) is a more powerful oxidizing agent in acetonitrile than ethanol.

The TTF–CuCl₂ System. Excess copper(II) chloride dihydrate in acetonitrile, a strong oxidizing agent, converted **1** to the yellow tetrachlorocuprate(II) salt (TTF)CuCl₄ (**4**). The resonance Raman spectrum of this material displays a strong band at 1306 cm⁻¹, characteristic of the TTF dication. Like the fluoborate salt, **4** is moisture sensitive, but it is sufficiently stable to be handled in air for short periods of time. The Cu(2p₃/₂) binding energy in **4** was 931.6 eV, indicating that it contains Cu(II).

A less highly oxidized material was obtained from TTF and CuCl₂·2H₂O in ethanol. The product (TTF)₃(CuCl₂)₅ (**5**) was isolated as a dark purple microcrystalline solid. The resonance Raman spectrum (Table IV) exhibited strong bands at 1298 and 1418 cm⁻¹, which indicates that **5** contains both TTF⁺· and TTF²⁺. Recrystallization of **5** from acetonitrile, without special precautions to exclude oxygen or moisture, produced very thin needlelike crystals of (TTF)₂CuCl₄ (**6**). The strong Raman band at 1414 cm⁻¹ shows that this is a chlorocuprate(II) salt of the TTF cation radical.

Additional structure information about the TTF²⁺ and TTF⁺· chlorocuprates **4** and **6** was obtained from a study of their magnetic susceptibility and electron spin resonance spectra. The corrected molar susceptibility of **4** down to 4 K followed the equation $\chi_{M_c}(T + 0.5) = 0.530$ and that of **6** was described by $\chi_{M_c}(T + 0.1) = 0.415$. The contribution to the magnetic susceptibility from the TTF cation radical in **5** is expected to be small since TTF⁺· often occurs as spin-paired dimers in the solid state. For example, (TTF)₃(BF₄)₂(**2**) is diamagnetic at 300 °C with a molar susceptibility of -4.2 × 10⁻¹⁰ cm³ mol⁻¹. Compound **6** showed a simple 2g value polycrystalline ESR spectrum.[29] The g values were $g_∥ = 2.053$ (5) and $g_⊥ = 2.322$ (5). Line widths were $\Delta H_∥ = 41$ G and

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Table IV. Resonance Raman Spectroscopic Data

compd (matrix)	excitation λ, Å	bands, cm^{-1} (rel intens)
(TTF)$_3$(BF$_4$)$_2$ (KBr)	5145	1931 (11), 1517 (29), 1455 (77), 1422 (79), 495 (100)
(TTF)(BF$_4$)$_2$	5145	144 (8), 1435 (14), 1340 (6), 1323 (100), 1302 (3), 788 (3), 642 (4), 550 (29), 519 (7)
(TTF)CuCl$_4$ (KBr)	4759	1847 (12), 1450 (14), 1306 (100), 1082 (8), 546 (29), 539 (33)
	5145	1450 (15), 1420 (8), 1306 (100), 1091 (5), 795 (5), 538 (32), 276 (10), 248 (7), 154
(TTF)$_3$(CuCl$_2$)$_5$	4579	1842 (10), 1580 (1), 1456 (16), 1418 (30), 1298 (100), 1087 (7), 1072 (14), 776 (4), 543 (62), 535 (72), 277 (4)
	5145	1921 (11), 1512 (5), 1454 (15), 1418 (100), 1298 (48), 540 (8), 532 (19), 506 (46)
(TTF)$_2$CuCl$_4$	4579	1926 (4), 1508 (3), 1414 (100), 1336 (14), 1327 (19), 509 (19), 488 (13), 309, 264 (16)
	5145	1926 (13), 911 (6), 1511 (18), 1485 (8), 1414 (100), 1327 (16), 754 (3), 512 (57), 484 (22)
(TTF)$_3$(CuBr$_2$)$_5$	4579	1822 (7), 1563 (2), 1448 (11), 1415 (16), 1296 (100), 1272 (3), 1081 (6), 1065 (6), 1054 (7), 769 (4), 536 (30), 527 (61), 271 (3)
	5145	1923 (12), 1503 (8), 1482 (7), 1449 (13), 1414 (100), 1296 (50), 1123 (15), 1023 (7), 884 (9), 536 (7), 529 (17), 503 (60)
(TTF)(CuBr$_3$)$_{0.4}$	4579	1512 (1), 1415 (100), 1032 (3), 757 (3), 311 (5), 262 (5)
	4880	1917 (2), 1512 (4), 1414 (100), 1031 (3), 756 (5), 624 (3), 516 (5), 503 (28), 312 (12), 127 (30), 100 (7)
	5145	2011 (2), 1982 (1), 1919 (21), 1512 (10), 1478 (8), 1441 (16), 1415 (100), 1004 (3), 756 (3), 502 (35), 97 (7)
(TTF)(CuBr$_3$) (KBr)	4579	183 (7), 1445 (14), 1424 (12), 1305 (55), 1297 (100), 1081 (6), 1068 (6), 1055 (6), 536 (34), 528 (61), 272 (7)
(TTF)$_3$Cu(NO$_3$)$_2$	4579	1416 (100), 1351 (8), 504 (13), 278 (15)
	5145	1908 (5), 1514 (5), 1444 (30), 1416 (50), 499 (100), 399 (8)
(TTF)(AuCl$_2$) (KBr)	4579	1507 (1), 1414 (100), 1149 (1), 1037 (3), 757 (3), 503 (1), 311 (6), 264 (6), 105 (3)
(TTF)(AuCl$_4$)$_2$	4579	1435 (15), 1419 (4), 1316 (67), 1076 (4), 790 (2), 642 (3), 551 (26), 370 (24), 347 (100), 326 (27), 181 (15)

$\Delta H_\perp$ = 43 G. These relatively narrow lines are indicative of exchange interactions between the copper(II) sites. The simplicity of the ESR spectral pattern and the spread of g values are strongly suggestive of an arrangement in which the individual metal ions are in a square-planar environment and the CuCl$_4$ planes are nearly parallel to one another. That is, the ESR data are most consistent with a chloride-bridged linear chain or a columnar structure although other geometries cannot be rigorously excluded.[30,31] For **4** the ESR parameters are $g_\perp$ = 2.123 (6), $g_\perp$ = 2.123 (6), $\Delta H_\parallel$ = 69 G, and $\Delta H_\perp$ = 175 G. The line widths are again suggestive of intramolecular spin exchange, but the g values are more consistent with a flattened tetrahedral geometry about copper.[32]

The weak band at 312 cm^{-1} in the Raman spectrum of (TTF)$_2$CuCl$_4$ may be tentatively assigned to a Cu–Cl mode, in which case D_{2h} coordination geometry about copper with bridging chlorine atoms is inferred. This frequency may be compared with 286 and 248 cm^{-1} in (CH$_3$NH$_3$)$_2$CuCl$_4$.[33] In the ammonium chlorocuprate, there are sheets of linked CuCl$_4$$^{2-}$ units with tetragonally elongated CuCl$_6$ octahedra.[34] Chloride bridges between copper(II) centers are quite common, as may be seen in Smith's review,[32] and the presence of this feature in **6** is neither unexpected nor inconsistent with the ESR data. The weak 276- and 248-cm^{-1} bands in the Raman spectrum of (TTF)CuCl$_4$ may be similarly assigned to Cu–Cl modes. This agrees with observation of bands at 280 and 253 cm^{-1} in Cs$_2$CuCl$_4$, which contains distorted tetrahedral CuCl$_4$$^{2-}$ ions[35] of approximately D_{2d} symmetry, and with the conclusions reached from consideration of spectral parameters. Due to the intensity variations with excitation wavelength, it is unlikely that the 276-cm^{-1} band is due solely to the ν_7 mode of TTF.

The availability of both ESR and magnetic susceptibility data provides an opportunity to assess the effective dimensionality in these TTF chlorocuprates. Since **6** exhibited narrower lines than did **4**, a stronger exchange field should prevail if their dimensionalities were the same. This is consistent with the observation that θ for **4** is indeed larger than that for **6**. Assuming that dipolar fields in **4** and **6** are about 200$_4$G and using previously published equations relating line widths, exchange, and dipolar fields,[36] we calculated a value for the exchange field based on three-dimensional interactions to be about 10^4 G, in reasonable agreement with the experimental θ values. Thus, we find significant intramolecular exchange fields in all three dimensions in these chlorocuprates. This is in contrast to [(CF$_3$)$_2$C$_2$S$_2$]$_2$Cu·(TTF), which was found to contain linear, one-dimensional Heisenberg chains.[12]

Many partially oxidized derivvatives of the type TTF$^{\rho+}$ (ρ < 1) are now known.[37,38] In this context, **5** is singular in that it is the first reported mixed valence compound containing both TTF$^+$ and TTF^{2+}. No ESR spectrum of **5** could be obtained down to liquid-nitrogen temperature, and the corrected molar susceptibility at 51 K was 1044 × 10^{-6} cm^3 mol^{-1}. These data suggest that the copper in **5** is mostly in the +1 state or that Cu(II) is present in a form in which the spins are tightly coupled. The X-ray photoelectron (ESCA) spectrum of **5** indicates that the copper is in the +1 oxidation state: the Cu(2p$_{3/2}$) core level binding energy was 928.7 eV, a reasonable value for Cu(I), and the shake-up satellites characteristic of Cu(II)[39] were not observed. In the absence of single-crsytal X-ray data, the structure of **5** and, in particular, the nature of the CuCl$_2$ moiety are not rigorously established. Two reasonable possibilities are a linear CuCl$_2$$^-$ and a chlorine-bridged structure, (CuCl$_2$)$_n$$^{n-}$. Only one example of linear CuCl$_2$$^-$ has been described,[40] although the gold analogue,

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$AuCl_2^-$, is well-known. The infrared spectrum of **5** fails to show the strong band in the low-frequency region expected for Cu–Cl stretching in $CuCl_2^-$ and found in $AuCl_2^-$ (vide infra). Further, halogen bridging is a pervasive feature of the structural chemistry of copper–halide systems,[32,41] and, more important for our purposes, (paraquat)Cu_2Cl_2 has been shown to contain a polymeric $(CuCl_2)_n^{n-}$ chain structure analogous to that of $BeCl_2$.[42] We suggest that a plausible representation of **5**, consistent with the Raman, infrared, ESCA, and magnetic susceptibility data, is $(TTF^{+\cdot})(TTF^{2+})_2[(CuCl_2)_n^-]_{5/n}$. It is important to note that **5** is not contaminated with **6**, for both compounds have distinctive infrared, Raman, and ESR spectra. The processes leading to the formation of **6** from **5** are clearly complex. It is probable that the TTF dication is reduced by adventitious water during the recrystallization procedure. However, additional reactions involving rupture of the $CuCl_2$ chains, disproportionation of Cu(I) to Cu(0) and Cu(II), and capture of $CuCl_4^{2-}$ by TTF cation radical to form $(TTF)_2CuCl_4$ also take place during the recrystallization process. Because of the polymeric nature of the $CuCl_2^-$ anion, **5** should not be regarded as biphasic, and it is significant in this regard that a material of similar composition and reaction chemistry can be prepared by oxidation of TTF with $CuBr_2$ in ethanol (vide infra).

The TTF–$CuBr_2$ System. The thiacarbon chemistry of this system is similar to that observed with copper(II) chloride. Differences arise because of the greater tendency of bromide to form bridging bonds between copper atoms as opposed to stabilization of discrete, mononuclear anions. Analogous to results with $CuCl_2$, addition of TTF to excess cupric bromide in ethanol afforded black, microcrystalline $(TTF)_3(CuBr_2)_5$ (**7**). The resonance Raman spectrum of **7** exhibited intense bands at 1414 and 1296 cm^{-1}, indicating the presence of both $TTF^{+\cdot}$ and TTF^{2+}. We suggest that this mixed-valence compound has the same composition as proposed for **5**, viz., $(TTF^{+\cdot})(TTF^{2+})_2(CuBr_2^-)_5$, and, indeed, their infrared and Raman spectra are very similar. Like its chloride analogue, **7** underwent extensive reorganization on attempted recrystallization. On cooling of a hot solution in acetonitrile, air-sensitive black microcrsytals of $(TTF)(CuBr_3)_{0.4}$ (**8**) separated. This compound was diamagnetic and exhibited no ESR signal. The $Cu(2p_{3/2})$ binding energies of **7** and **8** were 928.0 and 927.8 eV, respectively, and neither compound exhibited shake-up satellites due to Cu(II). Therefore, **8** is formulated as $TTF^{0.8+}(CuBr_3^{2-})_{0.4}$, which contains the structurally characterized[43] $CuBr_3^{2-}$ ion.

The resonance Raman spectrum of **8** (Table IV) shows bands at 1415 and 1441 cm^{-1} that can be assigned to ν_3 of $TTF^{+\cdot}$ and of $TTF^{\rho+}$ ($\rho < 1$), respectively. In $TTF^{\rho+}$, ν_3 correlates with the degree of partial oxidation, ρ, and, based on interpolation, is ~0.8 in **8**.[44] The $TTF^{+\cdot}$ in **8** is believed to arise from the laser-induced decomposition of $TTF^{\rho+}$, a process which we have also observed in $(TTF)_3(BF_4)_2$ and (TTF)(TCNQ). The composition also fits in with the simpler halide salts of $TTF^{\rho+}$ ($\rho < 1$), where lattice energy calculations indicate a dependence of the Madelung energy on ρ with a shallow minimum at $\rho \approx 0.8$.[45] Thus, in $(TTF^{0.8+})$-$(CuBr_3^{2-})_{0.4}$, the lattice energy of the TTF array would be near a minimal value and copper would be in the +1 valence state, an environment favored by the reducing bromide ion. The

broad, weak maximum at 1600 nm in the electronic spectrum may then be plausibly assigned to a $TTF–TTF^+$ intervalence charge-transfer process.

Cupric bromide forms a 1:1 adduct with acetonitrile,[46] and solvation of Cu^+ thus raises the redox potential of $CuBr_2$ relative to its value in ethanol. TTF undergoes a two-electron oxidation with cupric bromide in acetonitrile to yield light brown microcrystals of $(TTF)CuBr_3$ (**9**). The resonance Raman spectrum of this material showed intense bands at 1297 and 1305 cm^{-1}, consistent with its formulation as the $CuBr_3^{2-}$ salt of the TTF dication. A similar splitting of the ν_3 mode has been observed in a related metallotetrathiaethylene, $(TTF)HgCl_3$,[20] and this effect is may be due to two different kinds of TTF^{2+} ions distinguished by a small degree of electron transfer or to a site asymmetry-induced splitting. This subtle difference was not resolved in the electronic spectrum, which showed one strong band at 443 nm. The compound exhibited no ESR signal at room temperature, but at 78 K, a broad signal at $g \approx 2.1$, 570-G peak-to-peak width, was observed, probably due to traces of a Cu(II) impurity. The $Cu(2p_{3/2})$ binding energy (928.7 eV) is also typical of Cu(I). This compound is somewhat air sensitive, and, on deliberate exposure to air, a new peak grew in the ESCA curves at 929.9 eV with a shake-up satellite at 936.8 eV. These changes are attributed to oxidation of the Cu(I) to Cu(II).

The TTF–$Cu(NO_3)_2$ System. Oxidation of TTF with $Cu(NO_3)_2 \cdot 2H_2O$ in ethanol produced purple, microcrystalline $(TTF)_3Cu(NO_3)_2$ (**10**) which was converted to $(TTF)_2(NO_3)$ (**11**) on recrystallization from acetonitrile. The resonance Raman spectrum of **10** showed a band at 1446 cm^{-1} which decreased in intensity during exposure to the laser, behavior which is typical of $TTF^{\rho+}$ where, in this case, $\rho \simeq 0.7$. Efforts to obtain a Raman spectrum of **11** failed because of rapid decomposition in the laser beam. Nitrate bands were observed in the infrared spectra of **10** and **11** at 1350, 1358 cm^{-1} and 1240, 1250 cm^{-1}, respectively. The reaction of **1** and $Cu(NO_3)_2 \cdot 2H_2O$ in acetonitrile produced a yellow solid whose elemental analysis corresponded to $TTF(NO_3)_2$. However, this reaction was very difficult to control; in some experiments, a vigorous exothermic process with evolution of nitrogen oxides was observed. Some preparations of **10** were found to shock sensitive, and so further study of these organic nitrates was not pursued.

The TTF–$AuCl_4$ System. The increased oxidation potential of Au(III) in acetonitrile relative to ethanol as a solvent, as inferred from its reaction chemistry, parallels that of Cu(II). Addition of TTF to ethanolic $HAuCl_4 \cdot 3H_2O$ produced a dark red precipitate of diamagnetic $(TTF)AuCl_2$ (**12**). The resonance Raman spectrum of this material contained an intense band at 1414 cm^{-1}, diagnostic for $TTF^{+\cdot}$, suggesting that **12** is $(TTF^{+\cdot})AuCl_2^-$. The strong infrared absorption at 355 cm^{-1} is attributed to the ν_3 mode in linear[47] $AuCl_2^-$ and may be compared with 350 cm^{-1} in $(C_4H_9)_4NAuCl_2$.[48] The ESCA spectrum showed a single line at 83.6 eV for the $Au(4f_{7/2})$ level. This result rules out a chelate structure for **12** such as $[(TTF)_2Au]^+AuCl_4^-$ since the binding energies of Au(I) and Au(III) should differ by about 2 eV[49] and agrees with the Raman and infrared data. Oxidation with $HAuCl_4 \cdot 3H_2O$ in acetonitrile produced $(TTF)(AuCl_4)_2$ (**13**) as yellow flakes. The resonance Raman spectrum contained a strong band at 1316 cm^{-1}, as expected for TTF^{2+} derivative, and the infrared spectrum exhibited a strong band at 345 cm^{-1}, assigned to ν_1

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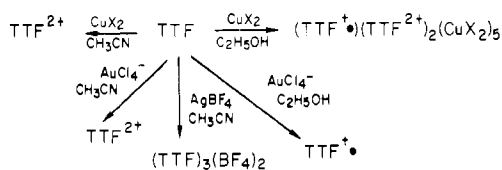
Figure 1. Oxidation of tetrathiafulvalene.

in $AuCl_4^-$.[50] In addition, the Raman spectrum shows bands at 347, 326, and 181 cm^{-1} which correspond to previously assigned $AuCl_4^-$ bands.[51] Thus **13** is the $AuCl_4^-$ salt of TTF^{2+}, $(TTF^{2+})(AuCl_4^-)_2$.

Discussion

We find that oxidation of TTF with cupric halides leads either to mixed-valence solids or to salts of the TTF dication, depending on the solvent employed. Gold(III) produces either $TTF^+\cdot$ or TTF^{2+}, and earlier work by Wudl[21] showed that silver(I) fluoborate provided $TTF^{0.7+}$. These reactions are summarized in Figure 1.

Reaction of TTF with cupric halides in ethanol yields mixed-valence materials of the type $(TTF)_3(CuX_2)_5$ (X = Cl, Br). Resonance Raman data disclose the presence of TTF in both the +1 and +2 oxidation states and the probable presence of a polymeric $(Cu^IX_2)^-$ counterion which nicely accounts for the observed copper:TTF ratios. Neither compound has successfully been recrystallized, and after dissolution in hot acetonitrile, $(TTF)_2CuCl_4$ (**6**) and $(TTF)(Cu^IBr_3)_{0.4}$ (**8**), respectively, were obtained. In this process, the copper(I) either disproportionates, is oxidized, or both, but the data at hand are insufficient to warrant conclusions about mechanisms of the reaction(s). In the case of $(TTF)_3(CuBr_2)_5$ (**7**), the copper remains in the +1 state, a result which can be explained on the basis of better stabilization of Cu^+ by bromide relative to chloride. The same factor probably accounts for the isolation of the copper(I) salt of TTF^{2+}, $(TTF)Cu^IBr_3$ (**9**), on oxidation of TTF with $CuBr_2$ in acetonitrile whereas cupric chloride led to a copper(II) derivative, $(TTF)CuCl_4$ (**4**). Rather similar chemistry was observed when $HAuCl_4$ was used as the oxidizing agent.

$(TTF)AuCl_2$ and $(TTF)_2AuCl_4$ were obtained in ethanol and acetonitrile solvents, respectively. Au(III) in ethanol is not a strong enough oxidizing agent to generate the TTF dication.

The electrical conductivity of the new tetrathiafulvalene halocuprates and -aurates was measured on compressed pellets (Table I). All were found to be insulators or semiconductors. While a detailed discussion of these data is not justified at this time, since only measurements on polycrystalline samples were performed, some conspicuous trends may be noted. First, the conductivity of $(TTF)_2CuCl_4$ is significantly higher than that of the dication analogue $(TTF)CuCl_4$, which parallels the trend in magnetic coupling between the Cu(II) centers in these compounds. Second, the conductivity of $(TTF)_3(CuBr_2)_5$ (**7**) is very much higher than in the $CuCl_2$ analogue **5**, and its is possible that this is reflected in the magnetic behavior; i.e., **7**, is diamagnetic but spins on **5** are not completely coupled. Finally, the conductivity of the partially oxidized derivative $(TTF)(CuBr_3)_{0.4}$ is much higher than that of the other copper and gold metallotetrathiafulvalenes which contain only TTF^{n+} ($n \geq 1$). It thus appears that, in these systems, the metal centers do not mediate strong electronic interactions between TTF ions. This results parallels those obtained with the TTF–bromine system. With complete charge transfer from the thiacarbon, the Coulombic repulsive forces prevent the

formation of uniform self-stacked structures in materials containing only TTF^+.[52]

Relationships between magnetic coupling and conductivity may be fortuitous, for, as noted by a reviewer, the former are determined by interactions between copper halide species and the latter by relative orientations, separation, and charge state of the TTF units in the solid.

Efforts to distinguish $TTF^+\cdot$ and TTF^{2+} by X-ray photoelectron spectroscopy were inconclusive. The sulfur 2s peaks in $(TTF)_3(CuCl_2)_5$ showed only marginal evidence of asymmetry, and two peaks could not be resolved. In **5**, **7**, and **8**, the half-widths of the 2s peaks were 2.5, 2.7, and 2.5 eV, respectively. Molecular orbital calculations on TTF and related compounds indicate that the electrons lost on oxidation come from molecular orbitals to which carbon AO's contribute extensively.[53] Electron density in the sulfur lone-pair orbitals is affected to a lesser degree, and so changes in the S 2s core energies are relatively small.

X-ray diffraction studies on $(TTF)(HgCl_3)^{20}$ and the 4,4',5,5'-tetrahydrotetrathiafulvalene complex $(H_4TTF)(HgCl_2)_3^{54}$ have demonstrated long (>3.1 Å) mercury–sulfur contacts and polymeric Hg–Cl chains. These results indicate that the sulfurs in H_4TTF and the TTF cation radicals are weaker nucleophiles than chloride toward Hg(II). Consequently, the coordination shell of mercury is completed by formation of Hg–Cl bridge bonds rather than by bonding to the thiacarbons. It is probable that a similar situation obtains in the TTF chloro- and bromocuprates, i.e., that these salts contain polymeric, halogen-bridged anions and that there is minimal bonding interaction between TTF and the metal in the counterions. This conclusion is also supported by the ESR data, for copper–sulfur bonding in the tetrachlorocuprates **4** and **6** would be expected to lead to considerably more distortion about copper and to lower g values than were observed.[55,56] Coordination numbers of 2 and 4 are normal for Au(I) and Au(III), respectively, and so it is probable that **12** and **13** contain isolated $AuCl_2^-$ and $AuCl_4^-$ ions; there is no evidence for strong gold–sulfur interactions in these salts. Wudl[5] has reviewed the structural possibilities for TTF transition-metal complex anions. These include materials in which the thiacarbon acts as either a neutral or cationic ligand or as a counterion. An example of the latter type of metallotetrathiaethylene has recently been reported. The novel compound $(TTF)_{0.61}Ir(CO)_2Cl_2^{57}$ is evidently a Krogman-type material with parallel stacks of $Ir(CO)_2Cl_2$ and TTF units and with no strong iridium–sulfur bonds. Because of the apparent low nucleophilicity of the TTF sulfurs, metallotetrathiaethylenes containing strong metal–sulfur bonds may be difficult to prepare. In agreement with ref 5, attempts to synthesize TTF coordination complexes from $(Ph_3P)_4Pt$ and $Mo(CO)_5THF$ have been unsuccessful.

Experimental Section

Tetrathiafulvalene was recrystallized from hexane–cyclohexane and then sublimed under vacuum. Copper(II) and gold salts were obtained commercially. Acetonitrile was distilled under nitrogen from P_2O_5. Magnetic susceptibility measurements were made down to liquid-helium temperature on a SQUID magnetometer. Conductivities were obtained at 9.5 GHz by the microwave cavity perturbation technique with use of compressed, polycrystalline samples. Electronic

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Table V. Analytical Data

compd	C	H	metal	S	X
3	19.0 (19.1)	1.1 (1.3)		33.9 (33.6)	B, 5.8 (6.0)
4	17.6 (18.0)	1.0 (1.0)	15.6 (16.1)	31.2 (31.4)	Cl, 34.6 (35.0)
5	16.8 (17.1)	0.9 (1.0)	24.8 (25.1)	29.9 (29.5)	Cl, 27.6 (28.0)
6	23.5 (23.9)	1.3 (1.3)	10.4 (10.2)	41.7 (41.4)	Cl, 23.1 (23.6)
7	12.5 (12.8)	0.7 (1.0)	18.5 (18.3)	22.2 (22.5)	Br, 46.2 (46.1)
8	22.1 (22.1)	1.2 (1.4)	8.0 (7.7)	39.3 (39.6)	Br, 29.5 (30.1)
9	14.2 (13.9)	0.8 (0.9)	12.6 (12.3)	25.2 (26.4)	Br, 47.2 (46.7)
10	27.0 (26.7)	1.5 (1.6)	8.0 (7.0)		N, 3.5 (3.3)
11	30.4 (30.0)	1.7 (1.7)		54.5 (53.2)	N, 3.0 (3.0)
12	15.3 (15.8)	0.9 (1.6)	41.7 (41.0)	27.1 (27.0)	Cl, 15.0 (15.4)
13	8.2 (8.1)	0.5 (0.6)	44.7 (45.0)	14.5 (14.1)	Cl, 32.2 (32.0)

spectra were obtained on Nujol mulls or as dispersions in KBr.

The RR spectroscopy of all samples was accomplished with excitation by a Coherent Radiation Model CR-8 Ar$^+$ laser. Spectra were collected with a 0.75-m Spex Model 1400-II double monochromator equipped with a cooled RCA C31034 photomultiplier tube and standard low-level threshold photon-counting-detection electronics. Further details concerning the collection optics and spectroscopic apparatus have been described earlier.[58] All spectra were obtained with rapidly spinning solid powder samples in a vacuum-sealed 5-mm o.d. Pyrex tube in order to minimize decomposition in the laser beam. Focusing and alignment of the sample were done quickly at very low laser power (<5 mW) so as to eliminate decomposition before the spectra are recorded. Typically, laser power levels of 40 mW were used. Spectra of **10** were obtained at ~15 mW with scans covering a 300–400-cm^{-1} region for a given sample.

X-ray photoelectron spectra were obtained with the use of Hewlett-Packard 5958C spectrometer and monochromatized Al Kα X-rays (E = 148.6 eV). The data were accumulated with a multichannel analyzer and were plotted in digital form. The C(1s) photoelectron line was taken as an internal standard with E_b = 285.0 eV.

EPR spectra were obtained with a reflection spectrometer operating at 9 GHz.

Unless otherwise indicated, reactions were carried out in Schlenk apparatus. The products were handled in an argon-filled drybox. Analytical data on the new materials prepared in this work are given in Table V. .

TTF(BF$_4$)$_2$ (3). A solution of 0.2 g (1 mmol) TTF in 10 mL of dry, deoxygenated acetonitrile was added dropwise with stirring to a filtered solution of 0.95 g (4 mmol) of Cu(BF$_4$)$_2$ in the same solvent under argon. After the addition was complete, white crystals began to separate. They were collected on a filter after 5 min and washed with diethyl ether (an orange contaminant is produced with extended reaction times) to give 0.15 g (42%) of product. Addition of ether to the filtrate gave an additional 0.2 g of less pure material. The salt turns brown on exposure to the atmosphere and was handled in a drybox.

Reduction of TTF(BF$_4$)$_2$. To 0.3 g of TTF(BF$_4$)$_2$ in 10 mL of dry, deoxygenated acetonitrile was added 0.1 of NaBD$_4$. After 24 h, the reaction mixture was filtered through Celite. The solvent was evaported and the residue extracted with 50 mL of boiling dichloromethane. This extract was evaporated and the residue sublimed. The ^{1}H NMR spectrum of the sublimate in CDCl$_3$ showed peaks at δ 6.38 and 6.07 in a 3:2 ratio. The higher field peak is assigned to 2,2'-dideuterobis(2,2'-dithiolyl) and that at δ 6.07 to TTF.

(TTF)CuCl$_4$ (4). A solution of 0.1 g (0.5 mmol) of TTF in 2 mL of acetonitrile was added with stirring to 0.34 g of CuCl$_2\cdot$2H$_2$O in 25 mL of acetonitrile. The golden yellow product which separated was collected on a filter, washed with 1 mL of acetonitrile and with pentane, and dried under high vacuum. The yield of **4** was 0.12 g (59%).

(TTF)$_3$(CuCl$_2$)$_5$ (5). A solution of 0.34 g (2 mmol) of CuCl$_2\cdot$2H$_2$O in 5 mL of ethanol was added with stirring to 0.1 g (0.5 mmol) of TTF in 15 mL of warm ethanol. The product was collected on a filter, thoroughly washed with ethanol, and vacuum dried to give 0.18 g (86%) of **5** as dark purple-black microcrystals.

(TTF)$_2$(CuCl$_4$) (6). A 0.1-g sample of (TTF)$_3$(CuCl$_2$)$_5$ was extracted in air with ten 50-mL portions of boiling acetonitrile. The extracts were filtered to remove a small amount of orange solid and concentrated to 20 mL on a rotary evaporator. Thin plates of (TTF)$_2$CuCl$_4$ separated. These were collected on a filter, washed with a small amount of acetonitrile, and vacuum dried. The yield was 0.08 g.

(TTF)$_3$(CuBr$_2$)$_5$ (7). A solution of 2 mmol (0.45 g) of cupric bromide in 10 mL of ethanol was added with rapid stirring in a thin stream to 0.1 g (0.5 mmol) of TTF dissolved in 10 mL of ethanol. The solid which separated was filtered off, washed thoroughly with ethanol, and then vacuum dried. The yield was 0.17 g (59%) of a maroon microcrystalline powder.

(TTF)(CuBr$_3$)$_{0.4}$ (8). A 0.16-g sample of (TTF)$_2$(CuBr$_2$)$_3$ was stirred with 30 mL of boiling acetonitrile. The hot solution was filtered and concentrated to 75 mL on a rotary evaporator to give 0.1 g of product as small, deep purple crystals.

(TTF)CuBr$_3$ (9). To 0.45 g (2 mmol) of CuBr$_2$ in 15 mL of acetonitrile was added dropwise with stirring 0.1 g (0.5 mmol) of TTF in 3 mL of warm acetonitrile. The brown, microcrystalline solid which separated was washed on a filter with six 10-mL portions of acetonitrile and then vacuum dried to give 0.25 g (100%) of product.

(TTF)AuCl$_2$ (12). A solution of 0.2 g (1 mmol) of TTF in 20 mL of warm ethanol was added with stirring in a thin stream to 0.4 g of HAuCl$_4\cdot$3H$_2$O in 15 mL of the same solvent. The dark red microcrystalline product was washed with 10 mL of ethanol and dried under high vacuum; yield 0.45 g (95%).

(TTF)(AuCl$_4$)$_2$ (13). A solution of 0.2 g of TTF in 8 mL of acetonitrile was added dropwise with stirring to 2.5 g of HAuCl$_4\cdot$3H$_2$O in 12 mL of acetonitrile. The initial TTF cation radical color was discharged, and bright yellow crystals separated as the addition progressed. The product was filtered under nitrogen, washed with dry acetonitrile, and dried under vacuum. The yield was 0.82 g (93%).

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