Copper Derivatives of Tetrathiafulvalene

By A. R. SIEDLE*,† G. A. CANDELA, and T. F. FINNEGAN
(*Institute for Materials Research, National Bureau of Standards, Washington, D.C.* 20234)
R. P. VAN DUYNE and T. CAPE
(*Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois* 60201)
and G. F. KOKOSZKA and P. M. WOYCIESJES
(*Department of Chemistry, State University of New York, Plattsburgh, New York* 12901)

Summary Oxidation of tetrathiafulvalene with $CuCl_2.2H_2O$ in ethanol produced the mixed valence metallotetrathiaethylene $(TTF)_3(CuCl_2)_5$ containing both $TTF^{+\cdot}$ and TTF^{2+}, which was converted into $(TTF)_2\ CuCl_4$ on dissolution in hot acetonitrile while the $CuCl_4^{2-}$ and BF_4^- salts of TTF^{2+} were prepared using $CuCl_2{\cdot}2H_2O$ and $Cu(BF_4)_2$ in acetonitrile; resonance Raman spectroscopy was used to probe the oxidation state of TTF in these copper metallotetrathiafulvalenes, and e.s.r. and magnetic susceptibility data indicate the presence of three-dimensional magnetic interactions in the TTF^+ and $TTF^{2+}\ CuCl_4^{2-}$ salts.

THE chemistry of tetrathiafulvalene (TTF) (**1**) and its partially oxidized derivatives has recently been recognized to be of considerable significance to the understanding of low dimensional materials.[1] Electronic interaction of the columnar TTF stacks in these solids is an important determinant of the electrical properties of this general class of materials. In most of the cases reported, partially as well as fully oxidized TTF derivatives have been prepared by the reaction of (**1**) with non-metal oxidizing agents such as Cl_2, I_2, and tetracyanoquinodimethane (TCNQ). Following the previous work in which transition metal derivatives of TCNQ were synthesized,[2,3] we now report a systematic study of novel TTF complexes[4] prepared by direct oxidation of (**1**) with transition metal halides. The copper derivatives of TTF show substantial chemical variations which depend on the solvent employed in their preparation and the nature of the counter-ion. We report the synthesis, electrical conductivities,‡ and characterization of TTF–copper chloride derivatives. In particular we note the utility of resonance Raman spectroscopy for the characterization of the TTF oxidation state. This information, along with e.s.r. and magnetic susceptibility measurements on the copper halide group, help to characterize these compounds.

Oxidation of (**1**) with $Cu(BF_4)_2$ in ethanol at room temperature produced $(TTF)_3(BF_4)_2$ whose *X*-ray powder pattern matched that of the salt obtained with $AgBF_4$.[1] In contrast, addition of ethanolic $CuCl_2{\cdot}2H_2O$ to TTF in the same solvent afforded deep purple, microcrystalline $(TTF)_3(CuCl_2)_5$,§ (**2**): λ_{max} (KBr) = 265, 415, and 780 nm; $\sigma = 1 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$; $\chi_c^M = 1044 \times 10^{-6}\ cm^3\ mol^{-1}$ at 51 K,¶ (*i.e.*, 208 c.g.s. units per mole of Cu). When (**2**) was

---

† Present Address: Central Research Laboratories, 3M Company, St. Paul, Minnesota 55101.

‡ Conductivities were measured on compressed pellets by the microwave cavity perturbation technique at 9·5 GHz.

§ Satisfactory analytical data were obtained for compounds (**2**)—(**5**).

¶ Magnetic susceptibility measurements were carried out down to liquid helium temperature.

dissolved in hot acetonitrile, further reaction occurred forming $(TTF)_2CuCl_4$, (**3**), as small black needles: λ_{max} (KBr) = 380, 500, and 880 nm; $\sigma = 5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$; $\chi_c^M(T + 0{\cdot}1) = 0{\cdot}415$. Direct oxidation of TTF with $CuCl_2{\cdot}2H_2O$ in acetonitrile yielded a yellow salt (TTF)-$CuCl_4$, (**4**): λ_{max} (KBr) = 310 and 445 nm; $\sigma = 5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$; $\chi_c^M(T + 0{\cdot}5) = 0{\cdot}530$. Finally, reaction of (**1**) with $Cu(BF_4)_2$ in acetonitrile gave $TTF(BF_4)_2$, (**5**): λ_{max} (KBr) = 380 and 540 nm.

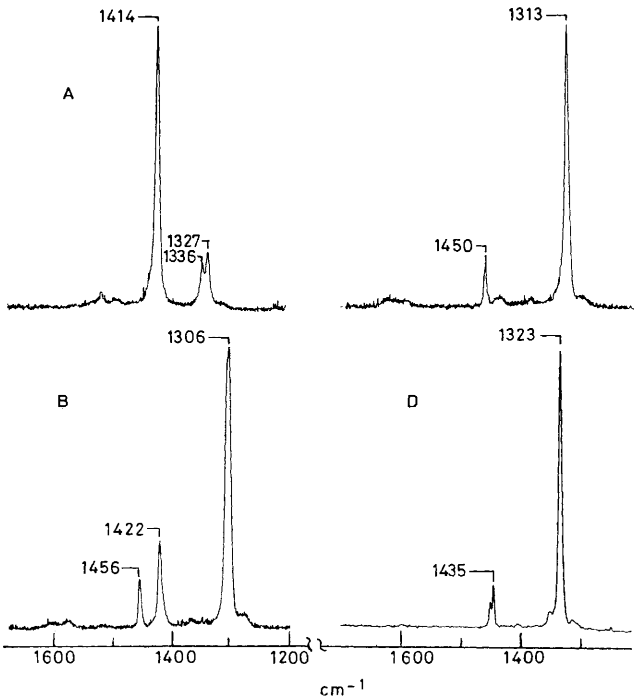

FIGURE. Resonance Raman spectra of the ν_3 C=C stretching mode of TTF in:
(A) $(TTF)_2CuCl_4$ (diluted with KBr, 4579 Å excitation, 40 mW laser power). (B) $(TTF)_3(CuCl_2)_5$ (diluted with KBr, 4579 Å excitation, 40 mW laser power). (C) $(TTF)CuCl_4$ (diluted with KBr, 4579 Å excitation, 40 mW laser power). (D) $(TTF)(BF_4)_2$ (neat powder, 5145 Å excitation, 10 mW laser power). All samples were sealed in evacuated 5 mm o.d. Pyrex tubes, spun, and irradiated at low laser power to avoid photodecomposition.

Resonance Raman and normal Raman spectroscopy can be utilized to probe the oxidation state of TTF *via* the frequency shifts which occur in its totally symmetric normal modes as it undergoes oxidation first to $TTF^{+\cdot}$ and then to TTF^{2+}.[5] Of the seven A_g normal modes in TTF, the ν_3 mode, which is predominantly the central C=C stretch, undergoes the largest frequency shift on oxidation. In solid TTF^0 $\nu_3 = 1515\ cm^{-1}$,[5,6] in solid TTFBr ν_3 for TTF^+ is at 1413 cm^{-1},[5] and in solid $TTF(BF_4)_2$ ν_3 for TTF^{2+} is at 1323 cm^{-1} (Figure, D). These data are qualitatively in accord with the magnitude and direction of the bond order changes from the central C=C as calculated by Zahradnik.[7] Thus by scanning the 1200—1600 cm^{-1} region of the Raman spectrum, it should be possible to identify the TTF oxidation state from these large frequency shifts. The Figure, A—C, illustrates the resonance Raman spectra of the TTF copper metallotetrathiaethylenes (**2**)—(**4**). On the basis of the ν_3 frequency, we conclude that (**2**) contains both $TTF^{+\cdot}$ and TTF^{++}, (**3**) contains predominantly TTF,$^{+\cdot}$ and (**4**) contains only TTF^{2+}.** To our knowledge, (**2**) is the first mixed valence compound resported which contains the TTF dication.

The e.s.r. line shapes of both $(TTF)_2CuCl_4$ and $(TTF)CuCl_4$ are characteristic of two *g* value systems.[8] The parameters for (**3**) are $g_{\parallel} = 2{\cdot}232(5)$, $g_{\perp} = 2{\cdot}053(5)$, $\Delta H_{\parallel} = 43$ G, and $\Delta H_{\perp} = 41$ G (half widths). The relatively narrow lines and the spread of *g* values suggest the presence of a parallel arrangement of square planar $CuCl_4{}^{2-}$ units which participate in intramolecular exchange. For (**4**) the e.s.r. data are $g_{\parallel} = 2{\cdot}476(5)$, $g_{\perp} = 2{\cdot}123(6)$, $\Delta H_{\parallel} = 69$ G, and $\Delta H_{\perp} = 175$ G. The linewidths are again suggestive of exchange but the *g* values are most consistent with a flattened tetrahedral co-ordination geometry about copper. From the equation relating linewidths, exchange fields, and dipolar fields,[9] a value for the exchange field based on three dimensional interactions was calculated to be *ca.* 10^4 G, in reasonable agreement with the experimental θ values. [Dipolar fields were assumed to be several hundred gauss in both (**3**) and (**4**)].

This work was supported in part by the Petroleum Research Fund administered by the American Chemical Society (G.F.K.), the National Science Foundation, (R.P.V.D.), and the Northwestern University Materials Research Center (R.P.V.D.).

(*Received*, 16*th September* 1977; *Com.* 975.)

** Further chemical and spectroscopic studies of the TTF dictation will be presented elsewhere.

[1] F. Wudl, *J. Amer. Chem. Soc.*, 1975, **97**, 1962; F. Wudl, D. E. Schafer, W. M. Walsh, Jr., L. W. Rupp, F. J. Disalvo, J. V. Waszczak, M. L. Kaplan, and G. A. Thomas, *J. Chem. Phys.*, 1977, **66**, 377; R. B. Somoano, A. Gupta, V. Hadek, T. Datta, R. Deck, and A. M. Herman, *ibid.*, 1975, **63**, 4970; R. B. Somoano, A. Gupta, V. Novotny, M. Jones, T. Datta, R. Deck, and A. M. Herman, *Phys. Rev.* B, 1977, **15**, 595; S. Etmad, *ibid.*, 1976, **13**, 2254; S. J. LaPlaca, P. W. R. Corfield, R. Thomas, and B. A. Scott, *Solid State Comm.*, 1975, **17**, 665.

[2] A. R. Siedle, *J. Amer. Chem. Soc.*, 1975, **97**, 5931.

[3] A. R. Siedle, G. A. Candela, and A. H. Kahn, *Bull. Amer. Phys. Soc.* 1977, **22**, 453.

[4] Donor–acceptor complexes containing (**1**) and metal chelates have been previously reported: L. V. Interrante, K. W. Browall, H. R. Hart, Jr., I. S. Jacobs, G. O. Watkins, and S. H. Wee, *J. Amer. Chem. Soc.*, 1975, **97**, 889.

[5] M. R. Suchanski and R. P. Van Duyne, manuscript in preparation; M. R. Suchanski, Ph.D. Thesis, Northwestern University, Evanston, 1977.

[6] A. J. Berlinsky, Y. Hoyano, and L. Weiler, *Chem. Phys. Letters*, 1977, **45**, 419.

[7] R. Zahradnik, P. Carsky, S. Hunig, G. Kiesslich, and D. Scheutzow, *Internat. J. Sulphur Chem.*, C, 1971, **6**, 109.

[8] D. W. Smith, *Co-ord. Chem. Rev.*, 1976, **21**, 93; B. J. Hathaway and D. E. Billing, *ibid.*, 1970, **5**, 143.

[9] R. Gaura, G. Kokoszka, K. Hyde, and R. Lancione, *Co-ord. Chem.* 1976, **5**, 105.