

Figure 1. Mass spectra vs. time of volatiles evolved in the thermal decomposition of $\text{Nb}_6\text{Br}_9\text{N}_7$: (a) N_2 ; (b) HBr . Part c: total ion current vs. temperature (the straight line shows the temperature gradient in the experiment).

of emptying the ampule with about 5% NaBr . No significant amounts of volatiles were collected in the pyrolysis of this compound.

Pyrolysis of compound I in the tortuous path assembly produced Nb_4N_3 . The condensable volatile products in this case were NH_3 , NH_4Br , and NbBr_5 . Chemical analysis of the residue showed 5.3% Br. This compares with 6.1% residual chlorine in the 800 °C product isolated by Grebtsova et al., who found that heating to 1000 °C eliminates the residual halide.

The pyrolysis of compound II showed some interesting behavior. The tortuous path assembly produced a residue with the X-ray pattern of Nb_4N_3 and a Br content of 5.2%, while the product of the pyrolysis in a single tube had the X-ray pattern of hexagonal NbN and a Br content of 1.6%. The effect of the experimental conditions in forming these two distinct phases was confirmed in additional experiments. The tortuous path assembly produced in a number of experiments a metallic coating in the hot portion of the assembly. A SIMS analysis of the coating showed Nb^+ , NbN^+ , and NbO^+ . Examination by transmission electron microscopy of the coating showed the diffraction patterns of NbN , Nb_4N_3 , and Nb_2O_5 . The crystallites had dimensions in the 10–40-nm range. The presence of oxide might be due to exposure to air or diffusion from the quartz substrate. The formation of NbN coatings by a chemical vapor deposition route is an interesting phenomenon. The conditions controlling this process have not been established, but, apparently, the vapor species NbBr_5 and HBr , isolated and identified by FTIR, in conjunction with thermal gradients have a significant role in the transport reaction.

In addition to NbBr_5 and HBr , nitrogen was also detected in a separate experiment by mass spectroscopic analysis of the volatiles. The NbBr_5 was condensed in the colder portions of the assembly and was not detected by MS. The profile of volatile production as a function of temperature is given in Figure 1. The hydrogen in the HBr collected in the decomposition of $\text{Nb}_6\text{Br}_9\text{N}_7$ is provided by a residual NH_4Br contamination of compound II. It is seen that nitrogen evolution occurs particularly at high temperatures while HBr is evolved within a narrow temperature range.

Conclusions

Niobium(V) bromide produces, depending on the experimental conditions, a series of ammonolytic intermediates showing metal to halide ratios of 2.0, 1.5, 1.0, 0.83, and 0.75. Particularly interesting from a chemical and structural point of view is the formation of a hexanuclear compound, $\text{Nb}_6\text{Br}_9\text{N}_7$. The intermediates are readily converted into acetylide derivatives of high metal content that yield upon thermal treatment niobium carbonitrides or mixed nitride-carbide phases. The amount of carbon introduced may be a variable susceptible to control given the variability of the metal to halide ratio in the intermediates.

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Electroconductive Tetrathiafulvalene Salt of Copper Iodide: $(\text{TTF})_{4/3}\text{CuI}_2$

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In our previous papers,²⁻⁴ we reported that copper(II) chloride and bromide function as excellent oxidants to form highly electroconductive tetrathiafulvalene (abbreviated as TTF) salts. The resulting compounds can be formulated as $[(\text{TTF})_n]^{+n}\text{Cu}^{\text{I}}\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$), in which each TTF moiety carries a fractional charge of $+1/n$. The electrical and magnetic properties vary markedly depending on the composition (i.e. the value of n), which can be readily controlled by using different halides and a variety of solvents. This flexibility in the design of different types of conducting complexes can be attributed to the difference in the stabilization of the Cu^{I} state of the halides in the various solvents. This observation has prompted us to investigate the synthesis and properties of the copper iodide-TTF salts. Copper(II) iodide, however, is not stable, and a TTF-CuI₂ complex cannot be prepared by the method that was used for the synthesis of the chlorides and bromides. In this study, we report the synthesis and physical properties of $(\text{TTF})_{4/3}\text{CuI}_2$. This compound has been characterized by IR and X-ray photoelectron spectroscopy (XPS) measurements.

Results and Discussion

Copper(II) acetate did not react with excess TTF in common organic solvents such as methanol, tetrahydrofuran, and acetonitrile, in contrast with the reactions of TTF with CuCl_2 and CuBr_2 . When an alkylammonium iodide was added to a mixture of copper(II) acetate and TTF in methanol, a reaction occurred immediately and $(\text{TTF})_{4/3}\text{CuI}_2$ was formed. In this reaction, the oxidant CuI_2 was prepared in situ. In the X-ray powder diffraction pattern of the product, a peak attributable to CuI was not found, indicating that the material was not contaminated by CuI . When tetrahydrofuran was used as a solvent instead of methanol, a TTF-CuI₂ complex was obtained. Its IR spectrum, however, indicated that the material was contaminated by an acetate. When acetonitrile was employed as a solvent, the resulting material did not contain copper but had the composition $(\text{TTF})_{1.0}$; this compound had been prepared by a reaction between TTF and I_2 .⁵ In the acetonitrile solutions, copper(II) ions act as oxidants, but

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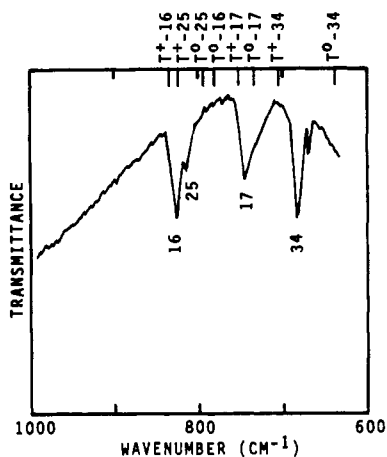


Figure 1. IR spectrum of $(\text{TTF})_{4/3}\text{CuI}_2$. The numbering of the vibrational modes is given after ref 8. Vibrational bands reported⁸ for TTF⁰ (abbreviated as T⁰) and for TTF⁺ (T⁺) are shown at the top for comparison.

acetonitrile molecules solvate the copper ions so strongly that iodide ions cannot enter into the first coordination sphere of the copper ions. Thus, the reaction in methanol yielded the new TTF-Cu complex $(\text{TTF})_{4/3}\text{CuI}_2$; this compound was subjected to the following physical measurements.

In the XPS spectrum of $(\text{TTF})_{4/3}\text{CuI}_2$, the copper $2p_{3/2}$ core electron peak was observed at a binding energy of 932.6 eV with a full width at half-maximum height (fwhm) of 2.3 eV. The binding energy is reasonable for Cu^I species: typical binding energies are 932.5–932.9 eV for Cu^I species and 935.2–935.4 eV for Cu^{II} species.⁶ Furthermore, the observed copper peak was not accompanied by the shake-up satellite that is characteristic of Cu^{II} species.⁶ Thus, the complex contains copper in the Cu^I state, the consequence of a redox reaction between Cu^{II} ions and TTF⁰ molecules. The sulfur 2p peak was located at a binding energy of 164.3 eV. The spectrum was slightly asymmetric with an fwhm value of 2.9 eV. The S 2p spectra of $(\text{TTF})\text{Br}_{0.7}$ and $(\text{TTF})\text{I}_{0.7}$ were reported to be significantly broader (fwhm = 2.7–3.1 eV) than those of TTF⁰ (fwhm = 2.1 eV) and TTF⁺ (fwhm = 2.5 eV).⁷ The peak in each of the halides was resolved into TTF⁰ and TTF⁺ components, and this indicated that the halides are mixed-valence complexes involving TTF⁰ and TTF⁺. The S 2p spectrum of $(\text{TTF})_{4/3}\text{CuI}_2$ was difficult to resolve into two component peaks. The fwhm value of 2.9 eV, however, is practically the same as that of the mixed-valence TTF halides; the TTF sulfur of this compound may be in a mixed-valence state. The iodine $3d_{5/2}$ peak was observed at a binding energy of 619.6 eV with fwhm = 2.4 eV.

The IR spectrum exhibited a very broad intense band that extended from 4000 to ca. 900 cm^{-1} . This band, which can be attributed to an electronic transition, masked the vibrational bands of TTF. Below the edge of the absorption band, some TTF vibrational bands were observed as shown in Figure 1. Some vibrational modes of TTF in its charge-transfer complexes show a significant frequency shift that depends on the TTF charge occupation. The vibrational modes observed for TTF⁰ and TTF⁺ are shown at the top of Figure 1.⁸ The bands observed for the iodide appeared at an intermediate position between the wavenumbers of the corresponding TTF⁰ and TTF⁺ bands. In a series of charge-transfer complexes in which intermolecular interactions are similar, a linear relation exists between the charge occupation of the constituent molecule and the frequency shift of a vibrational band.⁹ Our IR study³ of the series of $[(\text{TTF})_n]^+\text{Cu}^I\text{X}_2$ ($\text{X} =$

Table I. Physical Data for $(\text{TTF})_n\text{CuX}_2$ Prepared in Methanol: Powder Conductivity σ (S cm^{-1}) at 300 K, Activation Energy for Electrical Conduction E (eV), Thermoelectric Power Q ($\mu\text{V K}^{-1}$), Molar Magnetic Susceptibility χ (emu mol^{-1}) per Compound Formula, and Wavenumber (cm^{-1}) of the IR ν_{16} (CS Stretch) Band of TTF

X	n	σ	E	Q	$10^4\chi$	ν_{16}^a
I	$4/3$	0.4	0.11	10	-0.5	828 (830)
Br ^b	$5/3$	1.5	0.049	30	1.3	825 (823)
Cl ^b	2	14	c	35	3.3	816 (818)

^aThe wavenumber calculated from $792 + 51/n$ is given in parentheses. ^bReferences 2 and 3. ^cQuasi-metallic temperature dependence at high temperatures.

Cl, Br) has shown that the ν_{16} band (arising mainly from a CS stretch) shifts in a linear manner when plotted against the mean TTF charge density given by $+1/n$: the wavenumber of the mode can be calculated from the formula $792 + 51/n$ (cm^{-1}). If we assume the validity of this relation for the iodide, the wavenumber is calculated to be 830 cm^{-1} with $n = 4/3$, which is assumed from the compound formula: the calculated value agrees with the observed wavenumber within experimental error (Table I). This, together with the XPS results that have shown the Cu^I state of copper, suggests that the compound can be formulated as $[(\text{TTF})_{4/3}]^{+}\text{Cu}^I\text{I}_2$, in which each TTF moiety carries an equal fractional charge of $+3/4$.

The electrical conductivity of the compressed pellets was 0.4 S cm^{-1} , and that of the single crystals along the needle axis was 10 S cm^{-1} at 300 K. The temperature dependence of both conductivities, σ , can be explained by

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

with the activation energy $E = 0.11$ eV above ca. 200 K. The thermally activated temperature dependence is characteristic of semiconductors.

The compound showed a diamagnetic susceptibility equal to -0.5×10^{-4} emu mol^{-1} throughout the temperature range investigated, 100–300 K. Furthermore, no electron spin resonance signal was observed. When the two- or three-dimensional character of an electronic state is involved in a "one-dimensional" metal, the Landau–Peierls diamagnetism may appear in addition to the Pauli paramagnetism. On the basis of this model, Soda et al.¹⁰ interpreted the large diamagnetism (-1.92×10^{-4} emu mol^{-1}) that was observed for the low-temperature semimetallic phase of HMTSF-TCNQ (HMTSF = hexamethylenetetraselenafulvalene; TCNQ = 7,7,8,8-tetracyanoquinodimethan). The authors estimated the Landau–Peierls diamagnetism to be -2.32×10^{-4} emu mol^{-1} ; the difference, 0.4×10^{-4} emu mol^{-1} , between the observed and the calculated values was attributed to the Pauli paramagnetism. The Landau–Peierls diamagnetism may be a contributing factor to the noticeably large diamagnetism of the semiconductive $(\text{TTF})_{4/3}\text{CuI}_2$.

Table I shows the composition and physical properties of the $(\text{TTF})_n\text{CuX}_2$ complexes obtained from methanol solution. The physical properties are obviously related to the TTF charge occupation. The mean charge, $+1/n$, of TTF increases in the order chloride, bromide, iodide. In this order, TTF is oxidized to an increasing extent in the course of the complex formation. This is related to the relative stability of the Cu^I state of the halides in methanol. Attempts to prepare a TTF-CuF₂ complex were unsuccessful: no reaction occurred when tetrabutylammonium fluoride dissolved in tetrahydrofuran was added to a tetrahydrofuran solution of TTF and copper(II) acetate. CuF₂ prepared in situ did not oxidize TTF. This is attributed to the poor stabilization of the Cu^I state in copper fluoride. The selection of appropriate ligands is important, therefore, in the synthesis of

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highly conducting copper complexes.

Experimental Section

Preparation of $(\text{TTF})_{4/3}\text{CuI}_2$. When a methanol solution of tetrabutylammonium iodide (0.15 mmol/2 mL) was added to a mixture of copper(II) acetate hydrate (0.07 mmol) and TTF (0.15 mmol) in methanol (3.5 mL) with stirring under a nitrogen atmosphere, a dark purple powder separated out. After the resulting mixture was stirred for ca. 1 h, the precipitate was collected on a filter, washed with methanol, and dried under vacuum. Anal. Calcd for $(\text{C}_6\text{H}_4\text{S}_4)_{4/3}\text{CuI}_2$: C, 16.29; H, 0.91; I, 43.03; Cu, 10.8. Found: C, 16.23; H, 1.06; I, 43.09; Cu, 9.7. Single crystals were grown by diffusing a methanol solution containing $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ and TTF (1:2) and a methanol solution of tetrabutylammonium iodide. Very thin needles were formed with the typical dimensions $0.05 \times 0.05 \times 2$ mm.

Physical and Spectroscopic Measurements. The XPS spectrum was obtained by the use of a Vacuum Generators ESCALAB MK II spectrometer with Al $K\alpha$ X-rays (1486.6 eV). The binding energies were calibrated by assuming that carbon 1s electrons of a graphite powder, which was mixed with the sample, had a binding energy of 284.6 eV. The IR spectrum was recorded for Nujol mulls with a Perkin-Elmer 1420 spectrometer. The powder conductivity was determined by van der Pauw's four-probe method.¹¹ The crystal conductivity was measured along the needle axis by the standard four-probe method. Electrical contacts were made with Aquadag. The magnetic susceptibility was determined with the aid of a Faraday balance.¹² The molar susceptibility was corrected for diamagnetic contributions (10^{-6} emu mol⁻¹) from TTF (-99)¹³ and I⁻ (-52).¹⁴

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Vanadyl(IV)-Thallium(I)-205,203 Superhyperfine Coupling in Complexes with Pyruvate Kinase

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Pyruvate kinase is one of several enzymes that are known to require specific activation by monovalent cations.¹ Although K⁺ is the likely physiological activator for pyruvate kinase, several other species of monovalent cation bring about varying degrees of activation.^{2,3} The relative positions of the monovalent cation and the enzyme-bound divalent cation that is also required for activity of pyruvate kinase have been studied by NMR relaxation methods. These studies have been carried out with monovalent cations that have nuclear spins in conjunction with paramagnetic divalent metal ions such as Mn(II).⁴⁻⁹ The paramagnetic contributions to the longitudinal relaxation rates ($1/T_{1p}$) have indicated that in the presence of the substrate, phosphoenolpyruvate, the monovalent cation binds within 4.5-5.5 Å from the divalent

cation at the active site of the enzyme. Thallous ion is a good activator of pyruvate kinase,² and Tl⁺ has been useful as an NMR probe of the monovalent cation site because of the favorable magnetic properties of the two stable isotopes (²⁰⁵Tl, $I = 1/2$, 70.48%; ²⁰³Tl, $I = 1/2$, 29.52%).

Reuben and Kayne⁵ suggested that the substantially larger paramagnetic contribution to the transverse relaxation rate ($1/T_{2p}$) in measurements with ²⁰⁵Tl(I) and Mn(II) was possibly due to an appreciable ($A_{iso} = 0.85$ MHz) scalar superhyperfine coupling between the unpaired electrons of Mn(II) and the ²⁰⁵Tl nucleus. Vanadyl(IV) binds at the divalent cation site of pyruvate kinase,¹⁰ and the narrow EPR signals for enzyme-VO²⁺ complexes made it feasible to investigate superhyperfine coupling interactions between VO²⁺ and nuclear spin of monovalent cations by EPR spectroscopy. A resolved superhyperfine coupling between the unpaired electron spin of VO²⁺ and the nuclear spins of Tl⁺ has been observed with several different substrates or substrate analogues bound at the active site. Markham and Leyh¹¹ have independently observed a VO²⁺-^{203,205}Tl superhyperfine coupling of a similar magnitude in complexes with the enzyme S-adenosylmethionine synthetase.

Materials and Methods

Pyruvate kinase was prepared by the method of Tietz and Ochoa.¹² Solutions of the enzyme were equilibrated in a buffer containing 50 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid/tetramethylammonium hydroxide, pH 7.5, and 85 mM tetramethylammonium nitrate (buffer A) by gel filtration over a column (100 × 4 cm) of Sephacryl S-200 that was equilibrated and eluted with buffer A. Solutions of the protein were concentrated by using a collodion bag apparatus from Schleicher and Schuell. A stock solution of vanadyl sulfate was made up from the trihydrate (Aldrich Gold Label 99.999%). An aliquot from the stock solution was added to solutions of enzyme and substrate in buffer A that contained 1 mM dithiothreitol to minimize oxidation of the vanadyl ion. The amplitudes of the EPR signals for such solutions were stable for several hours. Spectra were recorded at 9.1 and 35 GHz with Varian spectrometers. Components of the g tensor and the ⁵¹V hyperfine tensor were obtained from the measured resonance fields by an iterative procedure based on the second-order expressions given by Chasteen.¹³

Results

Oxalate, a competitive inhibitor with respect to phosphoenolpyruvate¹⁴ binds at the active site of the enzyme as a bidentate chelate with VO²⁺.¹⁰ In buffer containing (CH₃)₄N⁺ as the monovalent cation, the EPR spectrum for solutions of the enzyme-VO²⁺-oxalate complex consists of a well-resolved powder pattern with $g_{||} = 1.926$, $g_{\perp} = 1.969$, $A_{||}(^{51}\text{V}) = 175 \times 10^{-4}$ cm⁻¹, and $A_{\perp}(^{51}\text{V}) = 67 \times 10^{-4}$ cm⁻¹. Addition of Tl(OAc) (see Figure 1) to a sample containing enzyme, oxalate, and vanadyl ion in the (CH₃)₄N⁺ buffer results in the appearance of well-resolved, satellite signals spaced symmetrically about the original signals. The separation of the satellite signals measured 34 ± 1 G (32×10^{-4} cm⁻¹) both for the parallel and for the perpendicular lines in the powder pattern. Splitting of precisely the same magnitude was observed in the spectra obtained at 35 GHz. These observations indicate that the satellite signals are due to a scalar superhyperfine coupling between the unpaired electron spin of VO²⁺

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