Communications to the Editor

Preparation and Properties of Some Tetrathiafulvalene Donor–Acceptor Compounds with Bis(dithiolene) Metal Complexes

Sir:

The identification of metal-like properties for the donor–acceptor compound tetrathiafulvalene–tetracyanoquinodimethane (TTF·TCNQ) and the continuing suggestions of potential superconductivity in such systems has generated considerable interest in this class of materials.[1] Efforts to understand the unusual properties of TTF·TCNQ and to explore the effects of chemical modifications in both the donor (TTF) and acceptor (TCNQ) molecules are currently underway in a number of laboratories.[2] We describe here the preparation and properties of some new compounds of this type in which a bis(dithiolene) (BDT) metal complex (Figure 1) replaces TCNQ as the acceptor. In the following paper we report some preliminary details regarding the unusual crystal structure of one of these materials.[3]

The close analogy between the BDT metal complexes and TCNQ has been noted previously.[4] Indeed, like TCNQ the neutral BDT metal complexes are known to form donor–acceptor compounds with organic molecules yielding in some cases materials with high electrical conductivities.[5] Except for a preliminary report of a $(\mathrm{TTF})\cdot\mathrm{NiS_4C_4(CN)_4}$ derivative prepared by reaction of $(\mathrm{TTF})\mathrm{Cl_2}$ with $\mathrm{Na_2NiS_4C_4(CN)_4}$,[6] materials derived from the combination of BDT complexes with TTF have not received much attention thus far. The flexibility of the BDT system inherent in the metal and ligand structure provides a unique opportunity to carry out a systematic study of structure–property relationships in TTF donor–acceptor compounds. We have undertaken such a study using neutral, diamagnetic BDT complexes which can be combined directly with TTF in organic solvents to yield donor–acceptor derivatives.

The compounds $\mathrm{TTF\cdot MS_4C_4(CF_3)_4}$ (M = Ni, Pt) were prepared in this manner using equimolar amounts of TTF[7] and $\mathrm{MS_4C_4(CF_3)_4}$[8] in benzene or acetonitrile solution. Single crystals of these materials can be grown from benzene solution as long black needles by slow diffusion of the reactants together in a solvent filled U-tube. On the basis of elemental analyses, conductivity in acetonitrile solution, electronic absorption spectra, and solid state magnetic susceptibility measurements, these compounds were identified as ionic charge transfer derivatives of the type $\mathrm{TTF^+MS_4C_4(CF_3)_4^-}$ in which one electron has been transferred from TTF to the BDT metal complexes. They are essentially electrical insulators with room temperature conductivities of $<10^{-9}$ ohm^{-1} cm^{-1}. The structures of these compounds and their unusual magnetic properties at low temperatures will be described in a subsequent report.

In contrast to these $\mathrm{CF_3}$ derivatives, which have been obtained only as 1:1 salts, mixtures of TTF with the compound $\mathrm{NiS_4C_4H_4}$[4,9] in acetonitrile yield different products depending on the proportion of TTF to $\mathrm{NiS_4C_4H_4}$ in solution. With a two → three times molar excess of TTF, a black crystalline solid is obtained on slow cooling for which elemental analyses, quantitative absorption spectrophotometry in acetonitrile, and proton NMR measurements in carbon disulfide solution suggest a $(\mathrm{TTF})_2(\mathrm{NiS_4C_4H_4})_3$ molecular formula. This material is difficult to obtain in pure form and its characterization is still in progress.

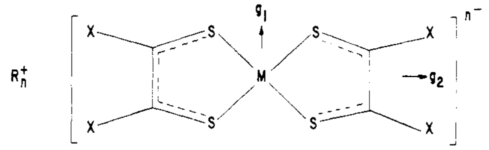

Figure 1. Molecular structure of the 1,2-ethylenebis(dithiolene) metal complexes where $\mathrm{R^+}$ = various organic and inorganic cations, X = H, $\mathrm{CH_3}$, CN, $\mathrm{CF_3}$, $\mathrm{C_6H_5}$, etc., M = Ni, Pd, Pt, Fe, Co, Cu, Au, etc., and n = 0, 1, 2. The observed directions for the principal g values, g_1 and g_2 are indicated; g_3 lies perpendicular to the plane of the molecule.

When the ratio of TTF to $\mathrm{NiS_4C_4H_4}$ is in excess of ~3:1, a compound, $(\mathrm{TTF})_2\mathrm{NiS_4C_4H_4}$, as large (~2 mm on a side), black single crystals with well-developed faces, is obtained on cooling. This compound has been fully characterized by complete elemental analysis, absorption spectrophotometry, proton NMR spectroscopy, magnetic susceptibility, ESR measurements, and a three-dimensional crystal structure analysis using X-rays. The electronic absorption spectrum, proton NMR, and conductivity measurements in acetonitrile indicate that this compound dissociates into a mixture of the neutral molecules in solution, consistent with expectations based on examination of the redox potentials for TTF[10] and $\mathrm{NiS_4C_4H_4}$[4] in this solvent. However, spectral studies, as well as magnetic susceptibility and EPR measurements, suggest that charge transfer does occur in the solid state to give a $(\mathrm{TTF})_2{}^+\mathrm{NiS_4C_4H_4}^-$ molecular composition.

The solid state absorption spectrum, obtained by transmission measurements on KBr pellets, shows a large negative shift in the position of the first visible absorption band relative to that in solution (from 13,900 to 11,100 cm^{-1}) as well as other changes which are consistent with the conversion of $\mathrm{NiS_4C_4H_4}^0$ to $\mathrm{NiS_4C_4H_4}^-$.[4] In addition, EPR measurements carried out on single crystals of $(\mathrm{TTF})_2\mathrm{NiS_4C_4H_4}$ evidence a strong, single, narrow line with g values at 20.4 K of $g_1 = 2.1217$, $g_2 = 2.0405$, and $g_3 = 1.9967$ (see Figure 1). The close similarity of these values to those previously observed for $\mathrm{NiS_4C_4H_4}^-$ [9] and for other $\mathrm{NiS_4C_4X_4}^-$ species[11] confirms the presence of this ion.

Static magnetic susceptibility measurements down to 4 K show behavior characteristic of a simple Curie paramagnet with no significant deviations from a linear $1/\chi$ vs. T relation and a Weiss constant of less than 1 K. However, the slope of the Curie plot gives a μ_{eff} of 1.67 BM/formula weight, indicating the presence of only *one* paramagnetic unpaired electron per $(\mathrm{TTF})_2\mathrm{NiS_4C_4H_4}$ formula unit, which, on the basis of the EPR measurements, is identified as that on the $\mathrm{NiS_4C_4H_4}^-$ ion.

The failure to observe an additional unpaired electron due to $\mathrm{TTF^+}$ ions in the solid may be understood on the basis of the crystal structure analysis which is reported in the following communication.[3] This structure determination indicates the presence of discrete $(\mathrm{TTF})_2$ dimers involving an eclipsed arrangement of two TTF units with particularly short S–S contacts. We suggest that these units may be viewed as $(\mathrm{TTF^+})_2$ molecular ions in which the $\mathrm{TTF^+}$ electrons are paired in a bonding molecular orbital encompassing both units. Indeed, one can envisage an appropriate combination of the b_{1u} π-orbitals, in which the unpaired electrons in TTF^+ presumably lie,[12] thus leading to a net bonding interaction in this configuration.

These $(TTF^+)_2$ units are connected in the structure by neutral TTF molecules along both the [010] and [001] directions in the monoclinic unit cell, resulting in a two-dimensional network of TTF units parallel to the (100) plane.

Four-probe dc conductivity measurements were carried out as a function of both temperature and crystallographic direction in this material. The conductivity was found to be thermally activated and to exhibit a linear log σ vs. $1/T$ dependence with a thermal activation energy of 0.23 ± 0.02 eV along both the [010] and [001] directions. The dc conductivities at 25° along [010] and [001] are 7.4×10^{-3} and 2.7×10^{-4} ohm^{-1} cm^{-1}, respectively, both of which are appreciably higher than the conductivities of either TTF[13] or $NiS_4C_4H_4$[4] alone. The conductivity perpendicular to the (100) plane has not yet been accurately determined but appears to be at least an order of magnitude lower than that in the (100) plane.

The interactions between TTF units suggested by the structural and property studies reported herein appear to be unprecedented both in the context of prior experience with TTF derivatives and with organic molecular solids in general. Further studies of these unusual materials are in progress.

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Crystal Structure of $(TTF)_2NiS_4C_4H_4$

Sir:

In the preceding paper[1] the synthesis and properties of some new donor–acceptor compounds of tetrathiafulvalene (TTF) with bis(dithiolene) (BDT) metal complexes are described. We report here preliminary information regarding the crystal structure of one of these compounds, $(TTF)_2NiS_4C_4H_4$.

The three-dimensional structure determination was made with crystals grown by slow cooling from acetonitrile solution and utilizing 1491 independent X-ray intensities collected on an automated GE 490 diffractometer with monochromatized Mo $K\alpha$ (λ 0.71069 Å) radiation.

The crystal system is monoclinic with $a = 25.80$ (2) Å, $b = 10.67$ (1) Å, $c = 9.990$ (5) Å, $\beta = 119.67$ (5)°, and space group $C2/m$. There are four $(TTF)_2NiS_4C_4H_4$ formula units per unit cell. The structure was solved by Patterson and Fourier syntheses and refined by least-squares calculations.

The locations of the centers of the molecules are shown in Table I. At the present level of refinement ($R = 0.12$ (F^2 basis)) all structural parameters (except for hydrogen atoms) are adequately known for a proper description of the arrangement of the constituent molecules. In particular the nickel and sulfur positions are indicated to be determined to within 0.01 Å. Further refinement incorporating additional data is underway to enable precise specification of intramolecular bond distances and angles involving the carbon and hydrogen atoms.

The structure consists then of three crystallographically distinct types of TTF units that occur in strips parallel to (100) and which alternate with strips containing $NiS_4C_4H_4$ units (Figure 1). The molecular planes of the crystallographically equivalent $NiS_4C_4H_4$ units are themselves parallel to (100) and the long dimension of the molecule is parallel to [001]. Two of the different TTF units are contained in a columnar stacking (Figure 2) along [010] with their planes at $y = 0$ (type I) and $y = 0.34$ and 0.66 (type II). While the molecular planes of these TTF units are all perpendicular to [010], those at $y = 0.34$ and $y = 0.66$ are rotated by about 60° with respect to those at $y = 0$. The two units at $y = 0.34$ and $y = 0.66$ are then in a fully eclipsed configuration with somewhat short intermolecular S–S contacts of 3.48 Å.

This unusual eclipsed arrangement of TTF units with S–S contacts appreciably shorter than the usual van der Waals separations is strongly suggestive of an appreciable intermolecular association. The significance of this "dimer unit," particularly in aiding the understanding of some of the unusual physical properties, is discussed in the preceding paper.[1]

A similar eclipsed arrangement of planar units has been observed in a crystal structure study of the $[MS_4C_4H_4]_2$ (M = Pd, Pt) complexes[2] where, interplanar S–S separations of about 3.0 Å occur to yield an approximately cubic array of S atoms. This close analogy in molecular structure also extends to the component planar units which differ

Table I

	x	y	z
Ni	± (0.197	0	0.170)
(center of $NiS_4C_4H_4$ unit)	± (0.697	½	0.170)
TTF (I)	0	0	½
	½	½	½
TTF (II)	± (0	0.337	½)
	± (½	0.837	½)
TTF (III)	0	½	0
	½	0	0