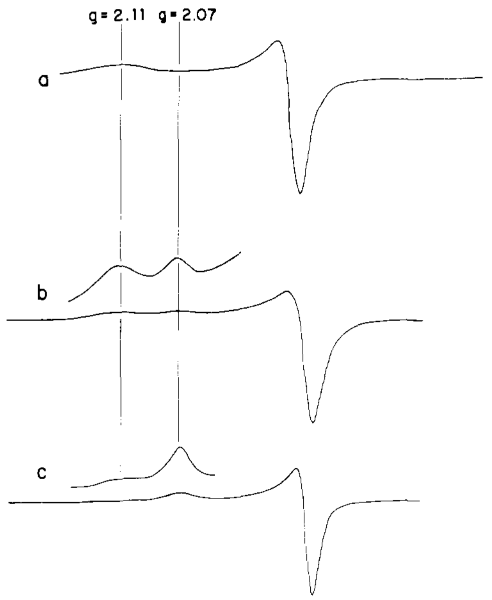

Figure 2. EPR spectra at 77 K of (a) O_2^- in Me_2SO; (b) O_2^- plus ZnTPP in Me_2SO; (c) O_2^- plus ZnTPP in benzene-Me_2SO (4:1).

$(O_2)]^-$ causes disappearance of the $g = 2.07$ peak as would be expected for displacement of coordinated O_2^- (see Scheme I). The shift of $g_\parallel$ to smaller values is expected when O_2^- is coordinated to a metal ion.[19] For example, O_2^- adsorbed on MgO has $g_\parallel = 2.077$.[19] EPR spectra of $[^{67}Zn(TPP)(O_2)]^-$[20] show a small but definite broadening (2-3 G) of the $g_\parallel$ peak. This is consistent with a highly ionic complex, i.e., little delocalization of the electron from O_2^- to Zn^{2+}.

Solid samples have been isolated from THF-hexane, which have elemental analyses consistent with the formulation K(dicyclohexyl-18-crown-6)$ZnTPPO_2$.[21] These blue powders are paramagnetic as evidenced by the fact that they have EPR spectra ($g = 2.00$) at 77 K which disappear reversibly upon warming to room temperature. Visible spectra of the dissolved solid show partial dissociation to Zn(TPP) as would be expected, since superoxide complex is formed in an equilibrium reaction. The instability of this material has hindered attempts to obtain quantitative magnetic data and IR spectra. Efforts are underway at this time to characterize these solids and to grow crystals that will be suitable for x-ray structural studies.

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References and Notes

(1) Abbreviations used in this paper: OEP, octaethylporphyrin; TPP, tetraphenylporphine; py, pyridine; TpivPP, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl) porphine; Me_2SO, dimethyl sulfoxide; THF, tetrahydrofuran; EPR, electron paramagnetic resonance.
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(15) λ_{max} (nm): Zn(TPP) (toluene) 422, 548, 587; $[Zn(TPP)(O_2)]^-$ (toluene) 433, 568, 608; $[Zn(TPP)(OH)]^-$ (dimethoxyethane) 432, 570, 611; $[Zn(TPP)(OC(CH_3)_3)]^-$ (toluene) 433, 569, 609; $[Zn(TPP)(OC_6H_5)]^-$ (benzene) 434, 565, 607. $[Zn(TPP)Cl]^-$ in CH_2Cl_2 gives 433, 569, 609 (see ref 12). The presence of dicyclohexyl-18-crown-6 does not affect the $[Zn(TPP)X]^-$ spectrum in any solvent used here.
(16) λ_{max} (nm): Zn(TPP)(py) (toluene) 428, 561, 600.
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(20) ^{67}Zn(TPP) (^{67}Zn, $I = \frac{5}{2}$) prepared from ^{67}ZnO (89.7% isotopic purity) from Oak Ridge National Laboratory.
(21) Anal. Calcd for $KZnC_{64}H_{64}N_4O_8$: C, 68.52; H, 5.76; N, 5.00; K, 3.49. Found: C, 68.43; H, 5.82; N, 4.85; K, 3.45.

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Tetrathiotetracenenickel Bis(ethylene-1,2-dithiolene). A New One-Dimensional Organic Conductor

Sir:

In the last few years the study of quasi-one-dimensional (1-D) conductors has become an important area of activity in current solid state physics research.[1] Presently, much of this interest is focused on organic π-donor-acceptor (D-A) systems with chain-like structures.[2] Despite the strong interest in such "1-D organic conductors", both the range and the absolute number of experimental systems currently available for detailed study are quite limited.

We now report the preparation and structural characterization of a new π-D-A compound which provides a unique opportunity to study 1-D electronic interactions in the presence of an internal magnetic subsystem. This compound has the empirical formula, $TTT_{1.2}NiS_4C_4H_4$, where TTT is tetrathiotetracene[3] and $NiS_4C_4H_4$ is nickel bis(ethylene-1,2-dithiolene).[4] It is the newest member of a class of π-D-A compounds derived from the interaction of bisdithiolene metal complexes with organic donor molecules[5] and the first of this class to exhibit a uniform, segregated stacking arrangement, characteristic of a 1-D organic metal.

It is obtained as small black crystals by slow cooling of a mixture of the two components in hot chlorobenzene solution.[6] Crystals measuring ca. 0.02 × 0.1 × 1.0 (mm) were used for four-probe dc conductivity measurements, EPR, and structural studies. Also, magnetic susceptibility measurements were made on an unoriented collection of these crystals using the Faraday method. The magnetic measurements show Curie-Weiss paramagnetism with an antiferromagnetic Weiss constant of ~5 K, indicative of essentially localized unpaired electrons. The magnitude of the Curie constant is that expected for one $g = 2$, $S = \frac{1}{2}$ electron per $TTT_{1.2}NiS_4C_4H_4$ formula unit. EPR measurements show only one line (~50 G at ~4 K) whose g-tensor is consistent with exchange-coupled $NiS_4C_4H_4^-$ units[4,5b] in the two orientations suggested by the crystal structure solution.

The crystal structure involves separate orthorhombic subcells for the two molecules with $a_{TTT} = 2a_{NiS_4C_4H_4}$ and $b_{TTT} = 2b_{NiS_4C_4H_4}$, but with c dimensions, corresponding to the needle axis of the crystal, in the ratio $c_{NiS_4C_4H_4}/c_{TTT} = 2.40$. The consequence is that for a given volume there are 1.2 mol-

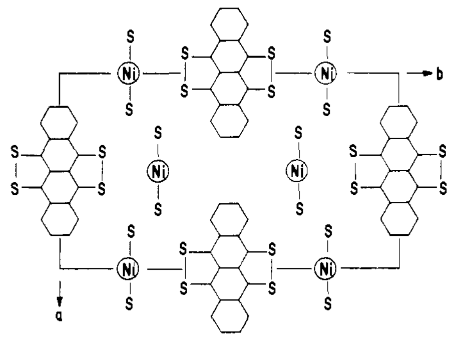

Figure 1. Projection of the $TTT_{1.2}NiS_4C_4H_4$ structure on the *ab* plane. Ni indicates positions of the Ni and two of the S atoms of the $NiS_4C_4H_4$ unit. These S atoms lie, respectively, above and below the Ni in the actual structure.

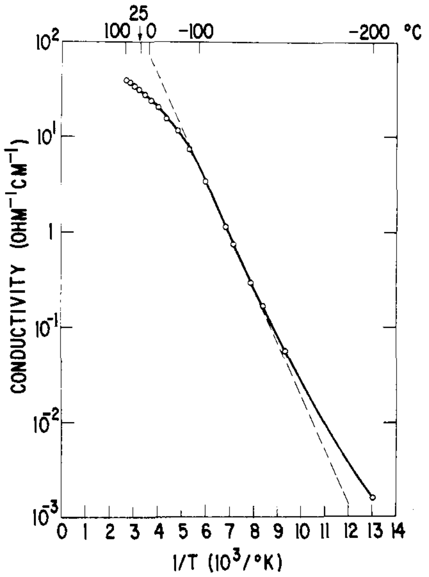

Figure 2. Conductivity (σ) of a $TTT_{1.2}NiS_4C_4H_4$ crystal as a function of temperature. The dashed line, which indicates the region of maximum slope of log σ vs. $1/T$, is drawn to illustrate the nonlinear character of the log σ vs. $1/T$ dependence.

ecules of TTT to 1.0 $NiS_4C_4H_4$. The complete structure has not yet been refined, but the structural parameters are known sufficiently well to specify the molecular arrangement. It is shown in Figure 1 in terms of the smaller subcell appropriate for $NiS_4C_4H_4$ for which a = 12.73 Å, b = 22.13 Å, and c = 8.73 Å, space group $C222_1$, with Z = 4 $NiS_4C_4H_4$ and 4.8 TTT. The plane of the TTT molecules is almost parallel to the *ab* plane with a uniform separation of 3.63 Å. The $NiS_4C_4H_4$ molecules are in planes perpendicular to b with two sulfur atoms in the *ab* plane and two above and below Ni. There are two distinct orientations for the C_2 axis which bisects the dithiolene chelate rings at ca. 45° to the c axis. There is no stacking of $NiS_4C_4H_4$ molecules nor are there any close contacts between them.

The apparently uniform stacking arrangement of TTT units along c is analogous to that found in $TTTI_{1.5}$[7] as well as that observed for other highly conductive organic D-A compounds.[2] The absence of structurally distinguishable TTT^+ and TTT units is suggestive of a delocalized electronic arrangement in the TTT substructure.

The temperature dependence of the dc conductivity (Figure 2) is also analogous to that previously found for other 1-D conductors below the peak in conductivity vs. T, which is associated with the cross-over from 1-D metal to Peierls semiconductor behavior in many of these compounds[2,8] In the case of $TTT_{1.2}NiS_4C_4H_4$, the conductivity reaches 30 ohm^{-1} cm^{-1} at 25 °C and continues to increase, with increasing temperature, up to the point of thermal decomposition of the sample (~180 °C), suggesting a cross-over to 1-D metallic conductivity behavior in a temperature range which is substantially higher than that typically found for 1-D metal systems.[2,8]

The results of the physical property measurements, in the context of the apparently uniform TTT stacking arrangement found in the structure, are strongly suggestive of a 1-D metal system with a highly correlated 1-D distortion[2,8] such that a gap in the electronic excitation spectrum exists up to the thermal decomposition point of the sample. The existence of such an energy gap could lead to the observed quenching of the TTT^+ unpaired spins as well as to the thermally activated conductivity behavior observed up to 180 °C.

The detailed nature of the 1-D distortions which produce this energy gap and the possible role of the $NiS_4C_4H_4^-$ spin subsystem in determining the unusually high temperature range for the metal-insulator transition are among the important questions which await more detailed studies on this compound.

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The [4]Annulene (Cyclobutadiene) System. The Tetrakis(trifluoromethyl) Derivative

Sir:

The chemistry of [4]annulene (**1**) continues to present an experimental challenge and to attract theoretical interest.[1] The full characterization of two simple derivatives (**2** and **3**) has recently been completed and provides unequivocal evidence