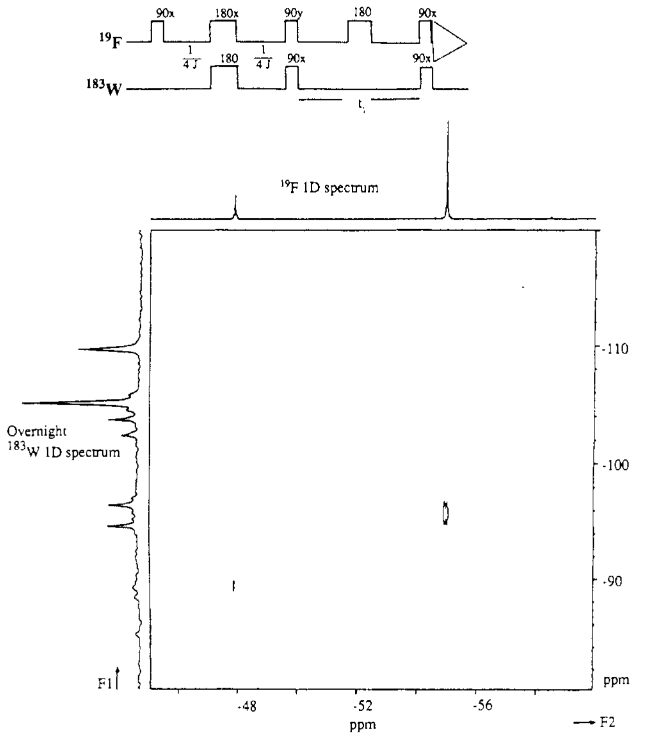

Figure 3. Magnitude model indirect (^{19}F–^{183}W) chemical shift correlation of ($H_2W_{12}FO_{39}$)H_5 (0.3 M in D_2O). The spectrum results from a 64 × 4096 data matrix. The delay time between scans was 2 s, and the number of scans was 32. Spectral width in F2 = 5617.98 Hz. Spectral width in F1 = 667.56 Hz. Apodization was with a sine bell squared in both dimensions. The total acquisition time was 2 hours. The reference for chemical shift scaling in F1 is 2 M Na_2WO_4 in D_2O.

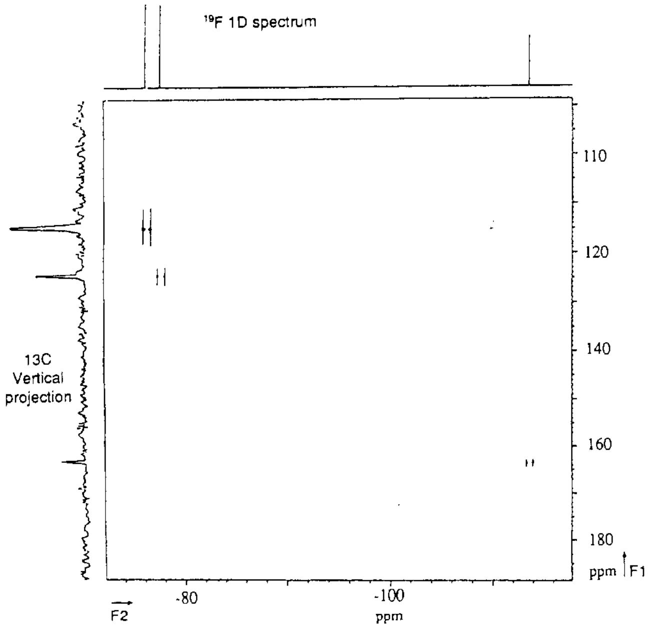

Figure 4. Magnitude mode multiple-quantum (^{19}F–^{13}C) chemical shift correlation of a mixture of fluorinated compounds in $CDCl_3$ (see text). The spectrum obtained with the four pulses sequence[14] results from a 256 × 8192 data matrix. The delay time between scans is 2 s, and the number of scans is 256. Spectral width in F2 = 17314.4 Hz. Spectral width in F1 = 10060.96 Hz. The spectrum was apodized by using an exponential multiplication of 2 Hz in F2 and 8 Hz in F1.

extra information that can be gained in such systems will be welcome for the biologist. Figure 4 is a good example of what can be done on a test mixture of 17 mM CF_3COOH, 20 mM CF_3CH_2OH, and 41 mM C_6H_5F in a $CDCl_3$ solution.

We clearly show that it is possible to extend easily the inverse experiments through the ^{19}F detection. From experimental time values comparison, it will be of particular interest for organometallic/inorganic chemists to study the transition-metal center X of fluorinated iron, osmium, or rhodium species where a *J*-(^{19}F–X) coupling is present. On the other hand, it seems to be also a very promising NMR tool for low concentration fluorinated metabolite solutions.

Experimental Section. All the experiments have been run on an AM400 instrument equipped with a 5-mm inverse probe head. The proton channel of this probe head had been retuned at the fluorine frequency (376.4 MHz). The fluorine frequency had been generated by a BSV7 broad-band transmitter and the tungsten frequency (16.67 MHz) via a BSV3/BX accessory with a 200-W pulsed amplifier (3–66 MHz).

For the (^{19}F–^{13}C) experiment, the BSV3/BX accessory of the spectrometer has been equipped with a 150-W pulsed amplifier (5–122 MHz) and the determination of the 90°(^{13}C) pulse value has been done directly on the mixture of the fluorinated compounds via the standard procedure.[11]

Registry No. ($H_2W_{12}FO_{39}$)H_5, 78829-53-5; tungstate, 12737-86-9; tungsten, 7440-33-7; fluorine, 7782-41-4.

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From Semiconductor–Semiconductor Transition (42 K) to the Highest-T_c Organic Superconductor, κ-$(ET)_2Cu[N(CN)_2]Cl$ (T_c = 12.5 K)

In this communication we report the discovery of an organic superconductor with the highest-T_c (12.5 K) recorded following the suppression of a semiconductor–semiconductor transition (42 K), which is accomplished by application of a minimal applied hydrostatic pressure (0.3 kbar). Comprehensive structure–property correlations for organic superconductors have been developed for the *isostructural* β-phase salts, β-$(ET)_2X$ (X^- = I_3^-, AuI_2^-, IBr_2^-).[1,2] Although several ambient-pressure superconductors are found in the κ-phase salts,[3,4] reliable structure-property correlations for these salts have not been developed due to the lack of *isostructural* κ-phase superconductors. The β- and κ-phase salts are characterized by very different structural packing motifs, viz., corrugated-sheet networks[5] of ET molecules and orthogonally arranged ET molecular dimers,[3] respectively. In this communication we report the discovery of a new κ-phase superconductor, κ-$(ET)_2Cu[N(CN)_2]Cl$, which is isostructural with the recently prepared ambient-pressure superconductor κ-$(ET)_2Cu[N(CN)_2]Br$ (T_c = 11.6 K)[4] and therefore has band dispersion relations and a Fermi surface[6] practically identical with those of κ-$(ET)_2Cu[N(CN)_2]Br$.

Synthesis, ESR Spectroscopy, and Crystallographic Identification. The new superconductor, κ-$(ET)_2Cu[N(CN)_2]Cl$, was prepared in the same fashion as the isostructural Br salt.[4] The

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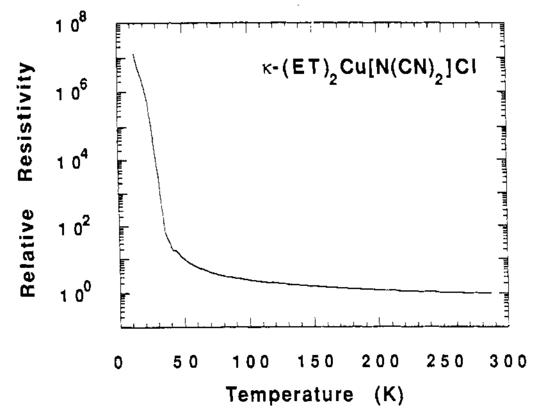

Figure 1. Plot of relative electrical resistivity at ambient pressure, $R(T)/R(300\text{ K})$, versus temperature for κ-(ET)$_2$Cu[N(CN)$_2$]Cl, indicating semiconducting behavior with a transition occurring at 42 K.

following chemicals were used during the electrocrystallization synthesis: ET, 10 mg (0.026 mmol, Strem); CuCl, 57 mg (0.58 mmol, Aldrich); PPh$_4$N(CN)$_2$, 158 mg (0.39 mmol).[13] The solvent used was 1,1,2-trichloroethane (TCE) and 10% (vol) absolute ethanol (to promote crystal growth). The current densities applied for different cells were between 0.1 and 0.5 μA/cm^2. The room-temperature ESR peak-to-peak line width is in the range 55–75 G, and the broad line width is comparable to that of the isostructural bromide salt and all other κ-phase salts.[14,15] The Cl and Br [V = 3317 (1) Å^3] derivatives are isostructural, with very similar atom positional parameters,[4] and the crystallographic data for the chloride salt at 298 K are as follows: a = 12.977 (3) Å, b = 29.979 (4) Å, c = 8.480 (2) Å, V = 3299 (1) Å^3, space group *Pnma*, and Z = 4.

Resistivity at Ambient Pressure. The four-probe resistivity, as a function of temperature at ambient pressure, of a single-crystal specimen of κ-(ET)$_2$Cu[N(CN)$_2$]Cl is illustrated in Figure 1. The room-temperature resistivity, $\rho(300\text{ K})$, for this specimen was ~0.5 Ω cm. With decreasing temperatures, the resistivity is weakly semiconductive with a thermal activation energy of ~12 meV below 300 K. Below 50 K, the resistivity is more strongly semiconductive with an activation energy of ~52 meV. The intersection of the two semiconductive regimes, as determined from least-squares fits of the data to exponential expressions of the type $\rho = \rho_0 \exp(E/kT)$, gives a transition temperature of ~42 K. At temperatures below 20 K, the resistivity behavior indicates another change in the temperature dependence, although this may be an artifact due to a saturation in the voltage compliance of the current-generating device. Resistivity measurements of several other single-crystal specimens gave very similar results in each case. Tests for superconductivity at ambient pressure by rf penetration depth measurements gave no indication of superconductivity to temperatures as low as 0.6 K.

It is of interest to compare the resistivity vs temperature behavior of this salt to that of the ambient-pressure superconductor κ-(ET)$_2$Cu[N(CN)$_2$]Br.[2c,4] The bromide-containing salt at ambient pressure initially shows very weak metallic resistive behavior from 300 to 225 K and then semiconductive behavior at lower temperatures with a thermal activation energy of ~6 meV; the resistivity reaches a maximum near 100 K, below which temperature it becomes strongly metallic and finally superconducting with a resistive onset of 12.5 K and zero resistance within instrumental limits at 10.5 K.

Superconductivity. Superconductivity was observed at pressures above 0.3 kbar. These pressures were generated in solid He by careful isobaric freezing of the He about the sample.[7] Superconducting onset temperatures were detected by use of an rf impedance method discussed earlier,[8] and temperatures were measured with a carbon glass thermometer affixed to the exterior of the pressure vessel immediately adjacent to the sample. Since the temperature is varied by adjusting the level of the experiment above a He bath, gradients can occur especially at pressures below 0.3 kbar, and these always result in a thermometer reading lower than the true sample temperature. We measured this gradient and corrected for it with an internal thermometer consisting of a chip of Nb in the coil with the sample. The Nb thermometer is corrected for pressure by use of the literature value of −0.2 K/kbar for dT_c/dP, and the gradient correction is negligible for pressures above 0.5 kbar. In this work, we use the identical apparatus in which the closely related compound κ-(ET)$_2$Cu[N(CN)$_2$]Br was studied under pressure.[9,10] This compound has the highest reported ambient-pressure transition temperature for an organic superconductor.[4]

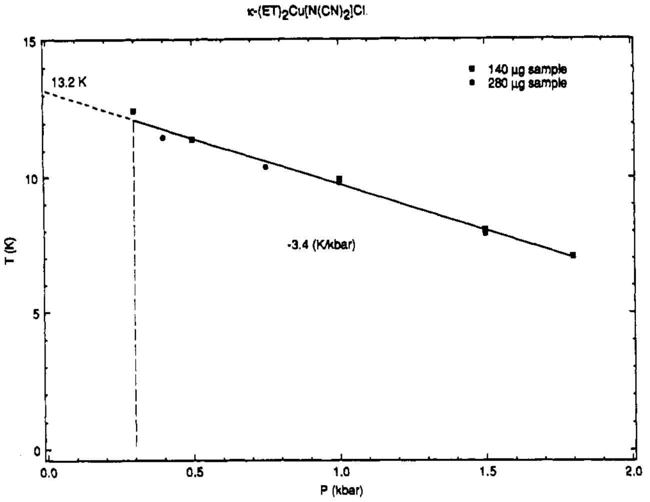

Figure 2. Superconducting transition temperature of κ-(ET)$_2$Cu[N(CN)$_2$]Cl versus hydrostatic pressure. The superconducting onset occurs at 12.5 K (P = 0.3 kbar), and the extrapolated T_c at ambient pressure is 13.2 K.

Our pressure results are summarized in Figure 2. A very weak superconducting diamagnetic response is detected at 0.2 kbar. At 0.3 kbar, a very strong superconducting signature is observed at 12.5 K. This is more than 1 K higher than that observed in the same apparatus for κ-(ET)$_2$Cu[N(CN)$_2$]Br at this pressure. As seen in Figure 2, T_c is strongly decreased with pressure at a rate of −3.4 K/kbar. This value is very similar to that observed in κ-(ET)$_2$Cu(NCS)$_2$, which has the largest pressure derivative of T_c reported for any material.[11,12] Extrapolation of T_c to ambient pressure indicates that κ-(ET)$_2$Cu[N(CN)$_2$]Cl would have a superconducting transition temperature of ~13.2 K.

Conclusions. We have discovered the first two ET-based isostructural κ-phase organic superconductors, κ-(ET)$_2$Cu[N-

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$(CN)_2]Br$ (T_c = 11.6 K) and κ-$(ET)_2Cu[N(CN)_2]Cl$ (T_c = 12.5 K, 0.3 kbar), respectively. As in the case of κ-$(ET)_2Cu[N(CN)_2]Br$, our band electronic structure calculations[6] show κ-$(ET)_2Cu[N(CN)_2]Cl$ to be a two-dimensional metal. Structure–properties correlations for κ-phase superconductors are now within reach and await the discovery of another isostructural superconducting salt. Extrapolation of T_c to ambient pressures for κ-$(ET)_2Cu[N(CN)_2]Cl$ indicates a T_c of ~13.2 K, and efforts are underway to stabilize this material in the superconducting ground state at ambient pressure.

Note Added in Proof. Four-probe resistance measurements with a Nb reference thermometer in series with the sample give T_c = 12.8 K at 0.3 kbar. We define T_c as the midpoint of the transition. The total transition width is less than 0.2 K at this pressure.

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Articles

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Chemistry in the Polar Intermetallic Host Zr_5Sb_3. Fifteen Interstitial Compounds

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Reactive (powder) sintering, arc-melting, vapor-phase-transport, and metal-flux methods have been explored for the synthesis of single-phase samples of compounds Zr_5Sb_3Z, in which an interstitial atom Z is bound in the centers of all zirconium trigonal-antiprismatic sites in the Zr_5Sb_3 host (Mn_5Si_3 type). Products of arc-melting are generally the least satisfactory as they are often substitutionally disordered or inhomogeneous and exhibit distinctly smaller lattice constants. Other procedures are described for the preparation of usually single-phase samples with Z = C, O, Al, Si, P, S, Co, Ni, Cu, Zn, Ge, As, Se, Ru, and Ag. The structures of two metal-flux products have been determined by single-crystal X-ray means ($P6_3/mcm$, $Z = 2$): Zr_5Sb_3Si, $a = 8.5409$ (5) Å, $c = 5.8248$ (7) Å, $R/R_w = 2.1/3.0\%$; Zr_5Sb_3Zn, $a = 8.6074$ (7) Å, $c = 5.8362$ Å, $R/R_w = 1.3/1.3\%$. The bonding of Z results primarily in small to moderate expansions of the relatively large zirconium cavity. The results of extended Hückel band calculations for Zr_5Sb_3 and Zr_5Sb_3S show how zirconium states and electrons are diverted from the broad conduction band to form strong Zr–Z bonds while the robust Zr–Sb and Zr–Zr bonding elsewhere in the structure is virtually unaffected.

Introduction

Cluster phases constructed from the early transition metals (T) exhibit some unusual and distinctive solid-state chemistries. The simplest to understand, and the most polar, are the many discrete cluster halides (X) formed from T_6X_{12} units. Metal-rich binary compounds formed between the same metals and the earlier chalcogens, pnictogens, and other main-group elements (M) still involve components with quite different valence-state energies, and the assignment of valence electrons to valence and conduction (or cluster) bands is usually quite straightforward.[2] However, the smaller fraction of M atoms means that even the binary compounds frequently occur in structures that are so condensed and complex that it is difficult to understand and discuss their structures, bonding, and chemistry directly without a theoretical band elaboration of each phase. Further reactions of most of these to form related ternary phases, interstitial or not, have not been systematically investigated beyond a few carbides, hydrides, etc.

Cluster halides constructed from group 3 or 4 metals have recently been found to exhibit a surprising property: all evidently require an interstitial element centered within each metal octahedron for thermodynamic stability.[3-5] Paralleling this, some metallic chalcogenide, pnictide, etc. phases with relatively simple cluster-based structures have been found to exhibit evidently analogous reactions. In these cases, a variety of third elements are taken up interstitially and without large structural changes so that electronic changes accompanying the reactions are easier to understand. The term "Nowotny phase" has been applied to some of these.[6]

One particular family, T_5M_3 phases with the Mn_5Si_3-type structure, have a longstanding reputation for their ability to bond a third interstitial element (Z) within T_6 octahedral cavities therein, or even to require the same for stability.[7-11] In fact, some

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