Communications

Sir:

Research on synthetic metals derived from the radical cation of bis(ethylenedithio)tetrathiafulvalene[1] (BEDT-TTF), herein abbreviated as "ET" (**1**), has been stimulated by the finding
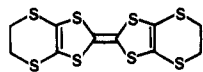

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BEDT-TTF or "ET"

of metallic conductivity to very low temperature[2] (1.4 K) in the 1,1,2-trichloroethane (TCE) solvated perchlorate derivative (ET)₂ClO₄(TCE)₀.₅ and the subsequent report of pressure-induced superconductivity[3] in unsolvated (ET)₂ReO₄ ($T_c \simeq$ 2 K at $p >$ 4 kbar). The unusual structure reported[4] for (ET)₂ClO₄(TCE)₀.₅ stressed the *absence* of columnar stacking, the most prominent feature in (TMTSF)₂X[5] conductors due primarily to short *intra*stack chalcogenide interactions, in favor of very short *inter*stack S–S interactions. This resulted in an isotropic two-dimensional "sheet network" of chalcogenide interactions between the ET molecules in (ET)₂ClO₄(TCE)₀.₅. Thus, it might be expected that even solvated (ET)₂X salts could constitute a new structural class of novel conducting materials and possibly even new superconductors. However, the likelihood that the only S-based organic *super*conductor, (ET)₂ReO₄, was substantially different in structure from the reported[6,7] (TMTSF)₂X (X = ClO₄⁻, ReO₄⁻, AsF₆⁻, PF₆⁻) superconductors appeared bleak with the preliminary report of a "TMTSF-like" structure and only the "possibility" of interchain S–S interactions in the ET salt.[3] The reported structural differences between metallic (ET)₂ClO₄(TCE)₀.₅ and superconducting (ET)₂ReO₄ could easily account for the differences in conducting behavior of these two systems. However, it is especially difficult to predict structure–conductivity behavior solely on the basis of room-temperature structural data. For example, variable-temperature (298 and 125 K) structural studies of the (TMTSF)₂X systems have demonstrated that there is a large and unpredicted anisotropy in *intra*- and *inter*chain Se–Se interactions, which strongly influence the electrical conductivity at low temperature, and also that precise structural correlations can be derived with use of the average interchain Se–Se distances derived at two temperatures for these systems.[7]

In order to shed light on the reported structural differences

(1) Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18.
(2) Saito, G.; Enoki, T.; Toriumi, K.; Inokuchi, H. *Solid State Commun.* **1982**, *42*, 557.
(3) Parkin, S. S. P.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, *50*, 270. In this report only the lattice parameters were given and V_c = 1565 Å³ (298 K). For (ET)₂ReO₄ we find that V_c = 1584 Å³ at 298 K and 1556 Å³ at 125 K. In a subsequent report in which no structural details are given (Parkin, S. S. P.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Voiron, J.; Carneiro, K.; Scott, J. C.; Greene, R. L. *J. Phys. (Paris)*, *Colloq. C3, Suppl. 6* **1983**, *44*, C3–791) the cell volume is given as V_c = 1589.3 Å³ in agreement with our results.
(4) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Enoki, T.; Inokuchi, H. *J. Am. Chem. Soc.* **1983**, *105*, 297.
(5) TMTSF is tetramethyltetraselenafulvalene.
(6) Bechgaard, K. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1.
(7) Williams, J. M.; Beno, M. A.; Sullivan, J. C.; Banovetz, L. M.; Braam, J. M.; Blackman, G. S.; Carlson, C. D.; Greer, D. L.; Loesing, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 643.
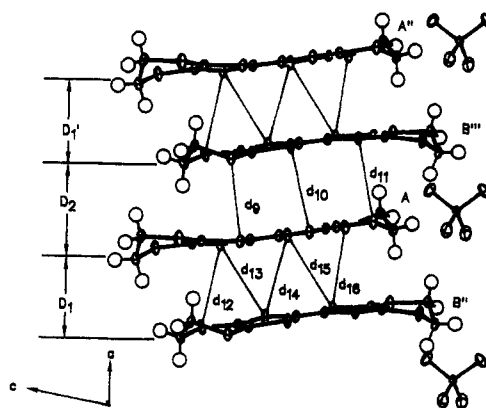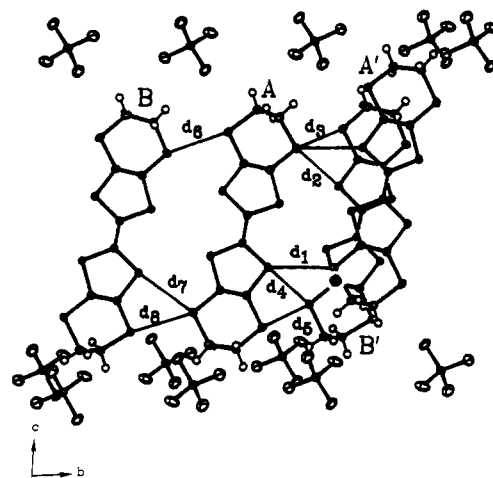
Figure 1. View of the intermolecular S–S interactions in (ET)₂BrO₄. The upper part indicates the *inter*stack S–S contact distances less than the van der Waals sum of 3.60 Å (298/125 K): d_1 = 3.581 (2)/3.505 (2), d_2 = 3.499 (2)/3.448 (2), d_3 = 3.583 (2)/3.483 (2), d_4 = 3.628 (2)/3.550 (2), d_5 = 3.466 (2)/3.402 (2), d_6 = 3.497 (2)/3.450 (2), d_7 = 3.516 (2)/3.434 (2), and d_8 = 3.475 (2)/3.427 (2) Å. The S–S contact distances, d_9–d_{16} (lower part) are, by contrast, all longer than 3.60 Å even at 125 K. In addition the loose zigzag molecular packing of ET molecules is such that they are not equally spaced, D_1 = 4.01/3.95 Å and D_2 = 3.69/3.60 Å. As a result of the (apparently) weak intrastack and strong interstack interactions, (ET)₂X molecular metals are structurally different from the previously discovered (TMTSF)₂X-based organic superconductors.[6] Almost identical S–S distances and interplanar spacings are observed in (ET)₂ReO₄ at both 298 and 125 K.

between (ET)₂ClO₄(TCE)₀.₅ and (ET)₂ReO₄, we have synthesized ET and electrocrystallized and structurally characterized (at 298 and 125 K) the tetrahedral anion derivative (ET)₂ReO₄ and the totally new and *isostructural* derivative

(8) BEDT-TTF was synthesized via the coupling reaction of 4,5-(ethylenedithio)-1,3-dithiole-2-thione (I). The reaction of Na with excess CS₂ in the presence of dimethylformamide yields 2-thioxo-1,3-dithiole-4,5-dithiolate, which was trapped by using 1,2-dibromoethane to give I in 26% yield. The coupling reaction of I in neat P(OEt)₃ gave red BEDT-TTF, which was twice recrystallized from CHCl₃. Electrocrystallization of (Et)₂BrO₄ was carried out in TCE at 1 μA/cm² current density with 2 mM ET and 0.1 M n-Bu₄NBrO₄, which was made from HBrO₄ titrated with Bu₄NOH and twice recrystallized from ethyl acetate. HBrO₄ was prepared with use of the literature procedure.[9] Anal. Calcd for Bu₄NBrO₄ (Found): C, 49.73 (49.76); H, 9.39 (9.69); N, 3.63 (3.64); Br, 20.68 (20.65); O, 16.56 (16.52). (Et)₂ReO₄ was prepared by electrocrystallization in a similar manner with use of Bu₄NReO₄ and ET. Anal. Calcd for n-Bu₄NReO₄ (Found): C, 39.01 (39.13); H, 7.37 (7.87); N, 2.84 (2.88); O, 12.99 (12.94, 13.07).
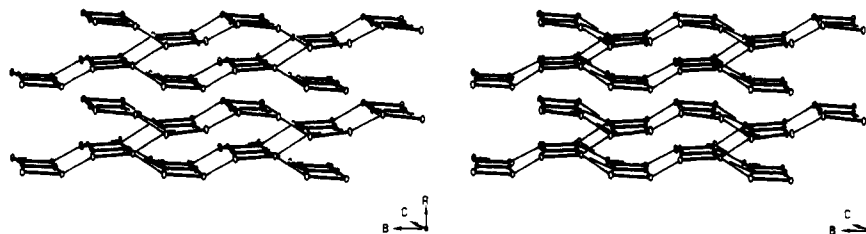
Figure 2. Stereoview of the short (<3.60 Å) intermolecular interstack S–S interactions in $(ET)_2ReO_4$ and $(ET)_2BrO_4$, which form a two-dimensional "corrugated sheet" network. This network is much different from that observed in $(TMTSF)_2X$ salts but similar to the network of interstack S–S interactions observed[4] in $Et_2(ClO_4)(TCE)_{0.5}$.

$(ET)_2BrO_4$.[8] Surprisingly, and contrary to the earlier report[3] for $(ET)_2ReO_4$, we have discovered that neither of these $(ET)_2X$ derivatives actually possess a TMTSF-like structure since (i) although these materials contain a loose zigzag packing arrangement of ET molecules, no significant *intra*stack (columnar) S–S interactions occur even after lattice shrinkage (298 → 125 K), resulting in nonparallel and nonplanar ET moieties (see Figure 1), (ii) numerous short *inter*stack S–S interactions occur, resulting in an unsuaul side-by-side stacking of ET molecules, and (iii) the resultant "corrugated sheet network" of interstack S–S contacts (see Figure 2) is different from that found in the $(ET)_2ClO_4(TCE)_{0.5}$ and $(TMTSF)_2X$ systems. Therefore, on the basis of these data from the only known unsolvated $(ET)_2X$ systems, (X = tetrahedral anion = ReO_4^-, BrO_4^-), it appears that they constitute a different *structural* class of organic metals, compared to the $(TMTSF)_2X$ systems, and hold the promise of a rich variety of electrical properties including potentially new superconductors (vide infra).

Diffraction Studies. Crystals of $(ET)_2ReO_4$ and $(ET)_2BrO_4$ were prepared by the electrochemical oxidation of ET in 1,1,2-trichloroethane solution in the presence of $(n\text{-}Bu_4N)X$ (where $X = ReO_4^-$ and BrO_4^-) as supporting electrolyte at a constant current (1.0 μA) and controlled temperature (23.4 °C).[8] In contrast to the single phases usually grown in the case of $(TMTSF)_2X$ systems, for ET the conditions of crystal growth lead to several different stoichiometries and distinct crystallographic phases. From TCE solution the BrO_4^- anion produces black metallic-appearing crystals of $(ET)_2BrO_4$-$(TCE)_{0.5}$ (thick plates), $(ET)_3(BrO_4)_2$ (thin plates), and $(ET)_2BrO_4$ (needles).[10] In contrast to the $(TMTSF)_2X$ systems, the tetrahedral anions are completely ordered in both structures at both temperatures (298 and 125 K). The ethylene carbon atoms of the ET molecules in $(ET)_2BrO_4$ are also ordered at both temperatures, and H atoms were located and their positional parameters refined.[11] That the $-CH_2$ groups are fully ordered even on the NMR time scale is also

evident because we are able to observe individual proton lines at a field of 7.5 kOe in a pulsed NMR experiment without the aid of any line-narrowing techniques. The proton spectrum is further resolved with applied pressure. The ESR susceptibility is consistent with metallic behavior over the temperature range 298–6 K. Below 6 K a magnetic phase transition is observed, which is suppressed to lower temperature with the application of pressure. Thus $(ET)_2ReO_4$ and $(ET)_2BrO_4$ are completely ordered at 298 and 125 K. The observation of crystallographic order as a necessary prerequisite to superconductivity in the only ambient-pressure organic superconductor, slow-cooled $(TMTSF)_2ClO_4$, is well established.[12]

As pointed out earlier, the ET molecules are decidedly nonparallel and nonplanar, and the loosely connected zigzag "stacks" are not equally spaced as is the case for $(TMTSF)_2X$ systems[13] (see Figure 1). The distortions of the ET molecules from planarity are such that the exocyclic carbon and sulfur atoms are bent away from the closest intrastack neighbor (see Figure 1). As a result, again in marked contrast to the case for the $(TMTSF)_2X$ salts, the intermolecular intrastack S–S contact distances, d_9–d_{16} (Figure 1), are large compared to the S–S van der Waals radius sum of 3.60 Å (shortest intrastack distance, d_9 = 3.645 (2) Å at 125 K), indicating nonspecific interactions in the quasi-stacking direction. However, short intermolecular *inter*stack S–S contacts, which are much shorter than the van der Waals S–S radius sum, are observed at low temperature, and the ET molecules thereby form a two-dimensional "corrugated sheet network" (see Figure 2). We speculate that one of the effects of applied pressure, which suppresses a metal–insulator transition at 81 K and is a prerequisite to superconductivity in $(ET)_2ReO_4$, is to substantially reduce both the intra- and interstack S–S distances, thereby increasing S–S overlap and adding increased "dimensionality" to the systems. However, at ambient pressures and with persistence to low temperatures (125 K) the primary S–S interactions are those *between* the molecular stacks compared to those within a stack in $(TMTSF)_2X$. Therefore, the unsolvated $(ET)_2X$ molecular metals appear to constitute a promising group of organic conductors and superconductors considerably different in structure from the known $(TMTSF)_2X$ conductors.

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(10) X-ray data were collected on a Syntex P2₁ diffractometer. The (E-T)₂ReO₄ crystals are triclinic, space group $P\bar{1}$, Z = 2, with unit cell parameters (298/125 K) a = 7.798 (5)/7.668 (2) Å, b = 12.579 (3)/12.583 (4) Å, c = 17.102 (6)/17.043 (5) Å, α = 73.37 (2)/73.27 (2)°, β = 80.35 (4)/81.24 (2)°, γ = 88.97 (4)/89.06 (2)°, and V_c = 1584 (1)/1555.9 (7) Å³; for (ET)₂BrO₄ a = 7.795 (2)/7.631 (4) Å, b = 12.613 (4)/12.564 (8) Å, c = 17.148 (5)/17.076 (9) Å, α = 72.97 (2)/73.21 (4)°, β = 80.44 (2)/80.49 (4)°, γ = 88.74 (2)/89.09 (5)°, and V_c = 1589.0 (8)/1545 (1) Å³. For (ET)₂ReO₄ (298/125 K) in the range 4.0 < 2θ < 50.0/60.0° 6325/10183 measurements were corrected for absorption (T_{min} = 0.65, T_{max} = 0.82) and averaged to give 5571/9120 unique data (R_{av} = 0.023/0.018); of these 4838/8065 reflections with F_{obsd} > 3σ(F_{obsd}) were retained. The initial structure solution, produced by MULTAN, was refined with full-matrix least squares to a final $R(F)$ = 0.041/0.032. In (ET)₂BrO₄ (298/125 K) 3434/9695 reflections in the range 4.0 < 2θ < 40.0/60.0° were corrected for absorption (T_{min} = 0.55, T_{max} = 0.80) and averaged to produce 2993/8672 unique data (R_{av} = 0.014/0.010). The structure parameters taken from the (ET)₂BrO₄ solutions were refined with full-matrix least squares to $R(F)$ = 0.034/0.039.

(11) Hydrogen atom positions were derived from difference Fourier maps and included in the least-squares refinement with fixed B_{iso} = 5.0 Å² (298 K) and B_{iso} = 3.0 Å² (125 K).

(12) Pouget, J. P.; Shirane, G.; Bechgaard, K.; Fabre, J. M. *Phys. Rev. B: Condens. Matter* **1983**, *27*, 5203.

(13) The ET molecules are nonplanar and nonparallel, and the interplanar spacings are (298/125 K) D_1 = 4.01/3.95 Å and D_2 = 3.69/3.60 Å for (ET)₂BrO₄ and D_1 = 4.01/3.97 Å and D_2 = 3.71/3.59 Å for (ET)₂-ReO₄. These were calculated from the average distance of the four inner sulfur atoms (S(1)–S(4) in molecule 1) from the planes of these atoms (S(11)–S(14) in molecule 2) in the ET molecules below and above along the stacking axis (a axis).

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Synthesis and Characterization of Carbonylpentacyanocobaltate(III)

Sir:

Most stable carbonyl complexes are formed with transition metals in a negative oxidation state or one of the lower oxidation states. A notorious exception is the carbonylpentacyanoferrate ion,[1] with iron in its +2 oxidation state. More recently the synthesis was reported of a binuclear Mn(III) complex in which two CO molecules act as bridging ligands.[2]

Because of our interest in the chemistry of various Co^{III}-$(CN)_5X^{n-}$ complexes, the existence of the iron (+2) carbonyl compound prompted us to attempt the synthesis of the isoelectronic $Co(CN)_5CO^{2-}$ complex ion, in which the cobalt atom is formally in the +3 oxidation state.

Almost sixty years ago Manchot and Gall reported on the synthesis of what they believed to be the $K_3[Co(CN)_5CO]$ complex.[3] Hieber et al., however, have proved that the procedure of Manchot and Gall leads to a mixture of K_3-$[Co(CN)_6]$ and $K[Co(CO)_4]$.[4] They also found that is was impossible to prepare the $K_2[Co(CN)_5CO]$ compound by interaction of CO with $Co(CN)_5OH_2^{2-}$ in aqueous solution.

Our first attempts to prepare $K_2[Co(CN)_5CO]$ in an analogous way as the complex $Na_3[Fe^{II}(CN)_5CO]$ were unsuccessful: as contrasted with the facile reaction of Fe-$(CN)_5NH_3^{3-}$ with CO in aqueous solution[5] we did not observe any reaction for several $Co(CN)_5X^{n-}$ complexes (X = H_2O, NH_3, Cl^-).

However, in a carbon monoxide saturated methylene chloride solution various $(n\text{-}Bu_4N)_n[Co(CN)_5X]$ complexes undergo a thermal or photochemical substitution reaction yielding the desired $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ complex. For the sake of convenience we used the thermal reaction of $(n\text{-}Bu_4N)_3$-$[Co(CN)_5Cl]$ with CO in CH_2Cl_2 at 298 K. The synthesis of the chloropentacyanocobaltate(III) complex was described earlier.[6] Prior to dissolution of the $(n\text{-}Bu_4N)_3[Co(CN)_5Cl]$ complex the solvent was saturated with CO in order to avoid the eventually interfering dimerization reaction of the starting complex.[7] The initial concentration of the complex was between 10^{-3} and 10^{-2} M. The solution discolors within a few minutes. As can be seen in Figure 1, the ligand field band of the original species vanishes completely and a new band appears at 310 nm. During the reaction the absorption spectra
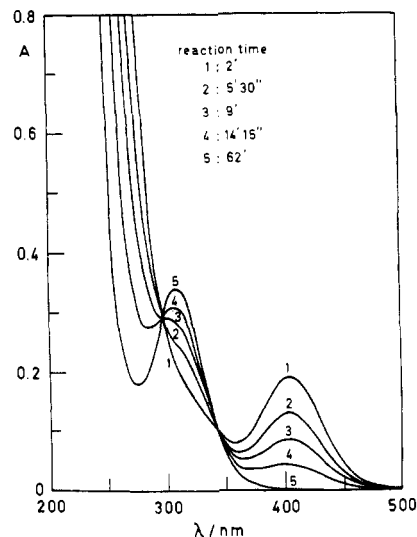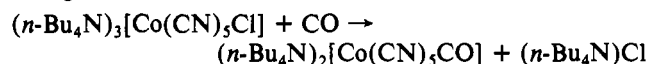

Figure 1. UV–visible spectra during the reaction of $(n\text{-}Bu_4N)_3[Co-(CN)_5Cl]$ with CO.

in the UV region evolve over two isosbestic points.

For the reasons enumerated below, we ascribe these spectral changes to the reaction

$$(n\text{-}Bu_4N)_3[Co(CN)_5Cl] + CO \rightarrow$$
$$(n\text{-}Bu_4N)_2[Co(CN)_5CO] + (n\text{-}Bu_4N)Cl$$

The reaction product is isolated over Sephadex LH 20 from the released $(n\text{-}Bu_4N)Cl$ by elution with CH_2Cl_2. The new complex is then precipitated as fine white crystals by the addition of diethyl ether and dried in vacuo over P_2O_5. The ultimate yield is about 80% due to some loss on eluting the complex over Sephadex.

The formula $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ for the isolated product was first confirmed by analysis of the cobalt content. Our experimental value of 8.47% agrees very well with the theoretical value of 8.40%. An elementary C, N, H analysis of our product, however, appears to be not very relevant due to the presence of two $n\text{-}Bu_4N^+$ cations.[5] A second argument for the above formula stems from the determination of the Co/CO ratio in a ^{14}CO-labeled sample of $(n\text{-}Bu_4N)_2[Co-(CN)_5CO]$. The Co/CO ratio was found to be 1.03/1.00. In addition we found that $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ in aqueous acid solution was quantitatively converted by UV irradiation into the $Co(CN)_5OH_2^{2-}$ ion, thus confirming the presence of the $Co^{III}(CN)_5$ moiety in the new product.

We have repeated the synthesis with several acidopentacyanocobaltate(III) complexes as starting material. In some cases (e.g. Cl^-, N_3^-) the reaction runs thermally. Other complexes such as $(n\text{-}Bu_4N)_2[Co(CN)_5py]$ are thermally inert, but upon irradiation into the ligand field band the reaction with CO proceeds efficiently. In all cases the same end product is obtained.

An aqueous solution of the carbonyl complex exhibits an absorption spectrum with a ligand field band at 307 nm ($\epsilon = 251$ M^{-1} cm^{-1}) and a charge-transfer band at 205 nm ($\epsilon = 25\,000$ M^{-1} cm^{-1}). The position of the ligand field band at 307 nm (310 nm in CH_2Cl_2) is in accordance with the somewhat higher ligand field strength of the CO ligand in comparison with the CN ligand. For the sake of comparison $(n\text{-}Bu_4N)_3[Co(CN)_6]$ has its first ligand field band at 311 nm in aqueous solution (320 nm in CH_2Cl_2).

The IR spectrum of $(n\text{-}Bu_4N)_2[Co(CN)_5CO]$ in a KBr pellet (Figure 2) shows a broad band at 2108 cm^{-1}, which we ascribe to the stretching of the ^{12}CO ligand. This band is accompanied by a much smaller band at 2061 cm^{-1}, which should be due to the ^{13}CO stretching. Generally this ^{13}CO band is found some 45 cm^{-1} below the ^{12}CO band.[8] In the

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(2) Ashmawy, F. M.; McAuliffe, C. A.; Minten, K. L.; Parish, R. V.; Tames, J. *J. Chem. Soc., Chem. Commun.* **1983,** 436.
(3) Manchot, W.; Gall, H. *Ber. Dtsch. Chem. Ges.* **1926,** *59,* 1056.
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