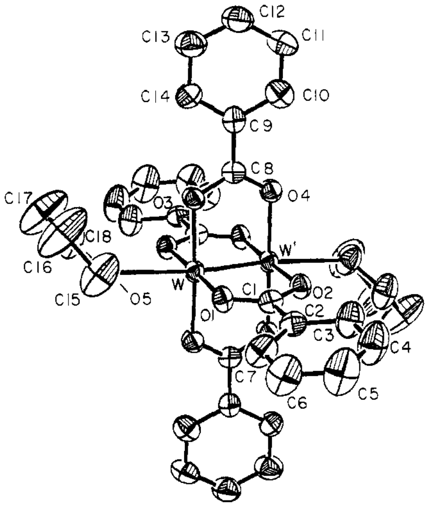

Figure 1. Structure of $W_2(O_2CC_6H_5)_4(THF)_2$ drawn by using the program ORTEP with each atom represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

$W_2Cl_4(PR_3)_4$ were discovered and characterized.[4,5] However, continued failure, despite many attempts, to prepare a $W_2(O_2CR)_4$ compound was striking—and also discouraging. It seemed impossible to believe that such compounds could not exist. Finally, in 1981 there appeared the first report[6] of the synthesis and characterization of such a compound, viz., $W_2(O_2CCF_3)_4$. Unfortunately, the preparative procedure is an arduous one, reported to give only 20% yield and, in our hands, never more than 5%.

It has been our view for several years that much of the difficulty with the preparation and stability of compounds containing the $W\overset{4}{-}W$ bonds is due to the weakness of the δ component of that bond and the consequent readiness with which oxidative addition of acid occurs. This view has recently received strong experimental support.[7,8] In accordance with this belief, we have been trying to synthesize $W_2(O_2CR)_4$ compounds under strictly nonacidic conditions. It was, indeed, only under such conditions that the synthesis of $W_2(O_2CCF_3)_4$ succeeded,[6] and as recent examples of the disastrous effect of acid, the reaction of the otherwise very stable compounds W_2(2,4-dimethyl-6-oxypyrimidinate)$_4$ and $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ with acids promptly and completely destroys the $W\overset{4}{-}W$ bonds,[4,9] leaving in one case a double bond and in the other case single bonds.

Our work has led to a procedure for the convenient preparation on a large scale of pure $W_2(O_2CC_6H_5)_4(THF)_2$. This substance is accessible enough and stable enough that it should become a desirable intermediate in further syntheses, which is unlikely to be the case with the trifluoroacetate.

In the preparation of $W_2(O_2CC_6H_5)_4(THF)_2$ all operations must be carried out in absence of air. In a representative procedure 5 g of WCl_4 was treated with 2 equiv of 0.4% sodium amalgam in 300 mL of THF at −20 °C. To the resulting gray-blue solution was added 4.45 g of sodium benzoate. This reaction mixture was allowed to warm to room temperature with constant stirring (about 0.5 h), and the resulting purple solution was filtered through Celite to remove sodium chloride and mercury. A 25-mL portion of the filtrate was transferred to a Schlenk tube and covered with 20 mL of hexane. Slow diffusion of the hexane into the THF solution over a period of 3 days to 1 week produced large, well-formed orange crystals. The yield of this highly crystalline product was about 0.35 g (ca. 55%). The solid is moderately sensitive to air and moisture but in solution the sensitivity is very great.

The compound crystallizes in space group $P2_1/c$ with 2 molecules in a unit cell of dimensions a = 9.511 (7) Å, b = 17.716 (7) Å, c = 10.843 (3) Å, and β = 109.52 (4)°. The structure was refined to $R_1 = 0.033$ and $R_2 = 0.042$ with 2011 reflections having $I > 3\sigma(I)$. The centrosymmetric molecule is shown in Figure 1. Its important dimensions, averaged for D_{4h} symmetry in the $W_2(O_2C-)_4(O)_2$ central portion of the molecule are W–W = 2.196 (1) Å, W–O(carbox) = 2.077 [6] Å, W–O(THF) = 2.628 (8) Å, ∠W–W–O(carbox) = 90.6 [3]°, and ∠W′–W–O(THF) = 169.7 (2)°. These distances may be compared with those in the molybdenum analogue,[10] $Mo_2(O_2CC_6H_5)_4$, which, in the above order are, 2.100 (1) Å, 2.107 [2] Å, 2.663 (6) Å, 91.8 [4]°, and 169.9 (1)°. As is very typical in such comparisons, the W–W bond length is about 0.10 Å longer, while the other dimensions are practically the same in the two compounds. The two crystallographically independent W–W distances in the trifluoroacetate were 2.207 (2) and 2.211 (2) Å.

After some additional physical and chemical studies are completed, a full report will be submitted.

Acknowledgment. We are grateful to the National Science Foundation for support. We thank Dennis Lay for the initial exploratory work and Dr. Graham N. Mott for his interest and advice.

Registry No. $W_2(O_2CC_6H_5)_4(THF)_2$, 82752-90-7.

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Synthetic Metals Based on Tetramethyltetraselenafulvalene (TMTSF): Synthesis, Structure (T = 298 and 125 K), and Novel Properties of $(TMTSF)_2H_2F_3$

Sir:

We report the synthesis and molecular structure as a function of temperature (T = 298 K and 125 K) of the unique tetramethyltetraselenafulvalene[1] organic radical cation salt $(TMTSF)_2H_2F_3$ (**1**). The relationship between the structure and the unusual physical properties of **1**, and of its sometimes superconducting congeners, is also discussed. The structural data for all 2:1 salts of $(TMTSF)_2X$, X = monovalent anion, reported to date indicate that they are *isostructural* (triclinic, space group $P\bar{1}$) and contain anions having octahedral or tetrahedral symmetry.[2] Despite their close structural simi-

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[1] TMTSF is $\Delta^{2,2'}$-bi-4,5-dimethyl-1,3-diselenolylidene.

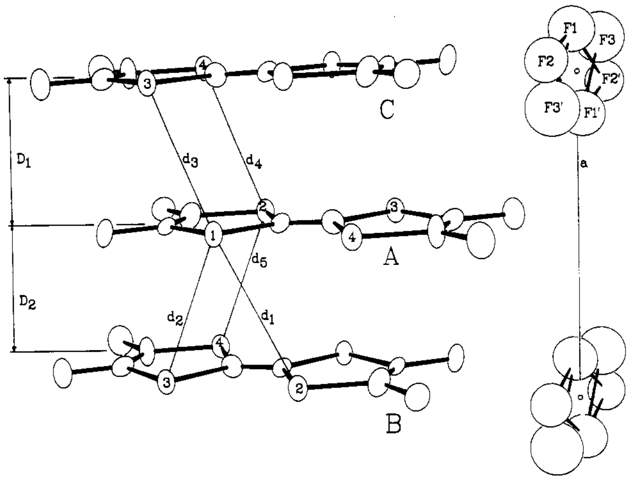

Figure 1. Molecular stacking in (TMTSF)$_2$H$_2$F$_3$. The four crystallographically independent Se atoms are labeled 1–4. The interplanar distances between molecules labeled A (symmetry: x, y, z), B ($1 - x, 1 - y, 1 - z$), and C ($2 - x, 1 - y, 1 - z$) are D_1 = 3.60/3.54 and D_2 = 3.60/3.53 Å and indicate that no significant dimerization of the molecular stacks occurs. All distances (D_n, d_n) given herein are at T = 298 and 125 K, respectively. The unique Se–Se contact distances[3] less than 4.1 Å are d_1 = 4.045 (1)/3.992 (1), d_2 = 3.965 (1)/3.891 (1), d_3 = 3.831 (1)/3.766 (1), d_4 = 3.889 (1)/3.818 (1), and d_5 = 3.903 (1)/3.832 (1) Å. The H$_2$F$_3^-$ anion is in disorder about the center of symmetry.[10]

larities, these salts exhibit a wide variety of metallic properties ranging from semi- to superconducting depending on the anion.[2] Although **1** is isostructural with previously reported triclinic derivatives, it is unique in that it (i) contains an anion lacking octahedral or tetrahedral symmetry, (ii) has the smallest unit cell volume (V_c = 671.2 (5), 650.0 (6) Å^3),[3] but *not* the shortest Se–Se contact distances yet reported, and (iii) exhibits X-ray diffuse scattering (XDS), a Peierls transition, and a metal–insulator (MI) transition at 65 K.[4] By contrast, (TMTSF)$_2$ClO$_4$ shows no XDS, has no Peierls transition, and is an ambient-pressure superconductor below 1.4 K.[5]

All (TMTSF)$_2$X salts reported to date contain a nearly uniformly spaced (zigzag) stack (along the high-conductivity a axis) of planar or nearly planar TMTSF molecules (see Figure 1), which also form an infinite "sheet network"[11] extending in the ab plane (see Figure 2).[2] The anions do not appear to play a significant role in the conduction process, which arises mainly through Se atoms via short Se–Se contacts.[6] However, by substitution of anions of different size, or by cooling of the salt in question, it is possible to vary the electrical properties by mimicking the effects of external pressure. Applied pressures of 6–12 kbar are, for example,

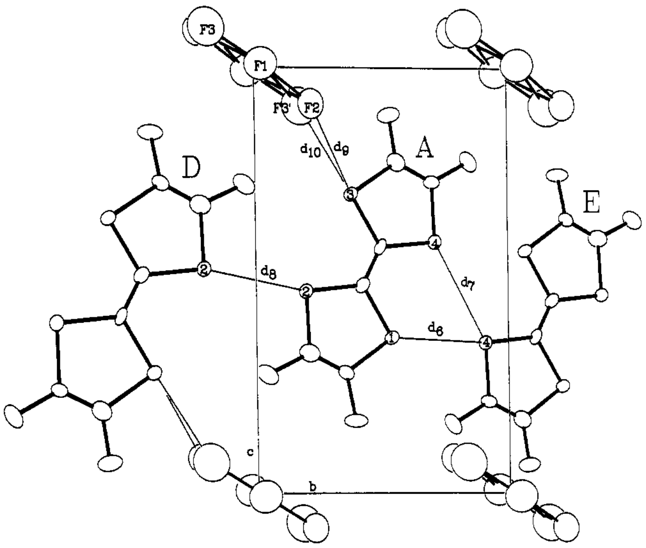

Figure 2. View of (TMTSF)$_2$H$_2$F$_3$ down the a^* axis, showing intermolecular *inter*stack Se–Se contact distances d_6 = 3.943 (1)/3.877 (1), d_7 = 4.029 (1)/3.941 (1), and d_8 = 3.816 (1)/3.735 (1) Å. The short Se–anion (Se···F) distances are d_9 = 3.34 (3)/3.30 (2) and d_{10} = 3.28 (3)/3.16 (2) Å. At both 298 and 125 K the *shortest* of the Se–Se distances are of the *inter*stack type. Symmetry operations for the three molecules: (A) x, y, z; (D) $2 - x, -y, 1 - z$; (E) $1 - x, 2 - y, 1 - z$.

sufficient to suppress metal–insulator transitions (which normally occur at $T < 20$ K) resulting in superconductivity in *all* octahedral anion (TMTSF)$_2$X salts (X = PF$_6^-$, AsF$_6^-$, and TaF$_6^-$).[2] However, salts containing tetrahedral anions exhibit MI transitions at much higher temperatures and may [T_{MI} = 182 K for (TMTSF)$_2$ReO$_4$[7]] or may not [T_{MI} = 40 K for (TMTSF)$_2$BF$_4$[8]] ever exhibit superconductivity at $T <$ 1 K under *applied* pressure.

Crystals of **1** were prepared by using a previously described procedure[2] and are triclinic, of space group $P\bar{1}$, with unit cell parameters[3] a = 7.209 (4)/7.068 (4) Å, b = 7.691 (3)/7.657 (4) Å, c = 12.837 (5)/12.753 (6) Å, α = 90.63 (3)/90.54 (4)°, β = 85.69 (3)/85.69 (5)°, γ = 71.15 (3)/70.91 (4)°, and V_c = 671.2 (5)/650.0 (6) Å^3.[9] The manner in which the H$_2$F$_3^-$ anions[10] cause the columns of the TMTSF stacks to form segregated sheets in the ab plane is illustrated in the figures. Within the errors of our measurements (<0.01 Å) the TMTSF stacks are *not* dimerized (see Figure 1). For comparison, in the ambient-pressure superconductor (TMTSF)$_2$ClO$_4$, D_1/D_2 = 3.63/3.63 Å (T = 298 K)[5] while, in (TMTSF)$_2$FSO$_3$, which shows a MI transition at 86–90 K, D_1/D_2 = 3.62/3.63 Å (T = 298 K) and 3.58–3.57 Å (T = 123 K).[11] Clearly, there

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(2) For a review see: Bechgaard, K. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1 and references therein. For the synthesis of (TMTSF)$_2$H$_2$F$_3$ 10 mL of a 10^{-3} M TMTSF solution in CH$_2$Cl$_2$ containing Ph$_3$BzPH$_2$F$_3$ was oxidized on a platinum rod (0.25 cm^2) with a constant current of 8 μA. After 60% conversion the resulting crystals were harvested and washed with dry CH$_2$Cl$_2$. Analytical data (C, H, N, Se) and this diffraction study are in accord with perfect 2:1 stoichiometry.

(3) Numerical results reported twice for (TMTSF)$_2$H$_2$F$_3$ herein refer to values derived at T = 298 and 125 K, respectively. The van der Waals radius sum for Se (Pauling) is 4.0 Å.

(4) Mortensen, K.; Jacobsen, C.; Bechgaard, K., private communication. Preliminary four-probe electrical conductivity studies of (TMTSF)$_2$H$_2$F$_3$ reveal a room-temperature conductivity of 200 Ω^{-1} cm^{-1} along the highly conducting a axis and that it is metallic down to 63 K where a MI transition occurs.

(5) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440.

(6) For a general, but very recent, review of the electrical and other physical properties of (TMTSF)$_2$X salts see: *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1–362.

(7) Jacobsen, C. S.; Pedersen, H. J.; Mortensen, K.; Rindorf, G.; Thorup, N.; Torrance, J. B.; Bechgaard, K. *J. Phys. C* **1982**, *15*, 2651.

(8) Bechgaard, K.; Jacobsen, C. S.; Mortensen, K.; Pedersen, H. J.; Thorup, N. *Solid State Commun.* **1980**, *33*, 1119.

(9) Three-dimensional diffraction data (3099 independent data at T = 298 K and 2304 such data at T = 125 K) for (TMTSF)$_2$H$_2$F$_3$ were collected on a Syntex P2$_1$ diffractometer over the range 4.0° ≤ 2θ ≤ 55° at 298 K and 4.0° ≤ 2θ ≤ 50.0° at 125 K. Intensity data were reduced in the usual manner and corrected for absorption (μ_c = 108.4/111.6 cm^{-1}). Fluorine atom positions of the H$_2$F$_3^-$ ion were derived from Fourier maps and refined (full-matrix least squares) along with atom positional parameters and anisotropic temperature factors for TMTSF to $R(F)$ = 0.070 (298 K) and $R(F)$ = 0.052 (125 K).

(10) The fluorine atoms of the disordered H$_2$F$_3^-$ anion are located at six positions *about* the center of symmetry each with a population of 50%. This is the first case in which an atom of the anion does not reside at the center of symmetry. The average F–F distances of 2.26 (6)/2.30 (4) Å may be compared with those found in the anion in KH$_2$F$_3$ (2.33 Å). See: Forrester, J. D.; Senko, M. E.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1963**, *16*, 58.

(11) Williams, J. M.; Beno, M. A.; Appelman, E. H.; Capriotti, J. M. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 319.

appears at this time to be no correlation between the degree of dimerization of the TMTSF stacks and the onset of a MI transition.

Very little is known regarding molecular structure changes in TMTSF derivatives at reduced temperature although such changes markedly influence electrical properties. For (TMTSF)$_2$FSO$_3$ (T = 298 → 125 K) the decrease in the intermolecular *inter*stack homoatomic Se contact distances (see Figure 2) is *twice* that of the *intra*stack separations.[11] Essentially identical findings are reported for (TMTSF)$_2$ReO$_4$.[7] In **1** the changes (T = 298 → 125 K) in intermolecular *intra*stack Se–Se separations are nearly the same as those in (TMTSF)$_2$FSO$_3$ and (TMTSF)$_2$ReO$_4$ while the corresponding *inter*stack separations decrease approximately half as much in these two salts. For the homoatomic *inter*chain Se contact distances (see d_6, d_7, and d_8 in Figure 2) the ordering (T = 298 K) of these separations for different anions is

d_6: $\mathrm{FSO_3^-} < \mathrm{ReO_4^-} < \mathrm{H_2F_3^-}$
d_7: $\mathrm{ReO_4^-} < \mathrm{FSO_3^-} < \mathrm{H_2F_3^-}$
d_8: $\mathrm{FSO_3^-} < \mathrm{H_2F_3^-} < \mathrm{ReO_4^-}$

However, at reduced temperature (125 K) all three separations are ordered: for $d_{6,7,8}$, $\mathrm{FSO_3^-} < \mathrm{ReO_4^-} < \mathrm{H_2F_3^-}$. A comparison of reported unit cell volumes (T = 298 K) for various (TMTSF)$_2$X derivatives indicates that the H$_2$F$_3^-$ salt is the smallest yet reported with the order being $\mathrm{H_2F_3^-} < \mathrm{BF_4^-} < \mathrm{ClO_4^-} < \mathrm{FSO_3^-} < \mathrm{BrO_4^-} < \mathrm{ReO_4^-} < \mathrm{PF_6^-} < \mathrm{AsF_6^-}$. Clearly, although the H$_2$F$_3^-$ derivative has the smallest unit cell volume of any yet reported, this does not result in the shortest interchain Se–Se contact distances. This result is in marked contrast to expectations in these systems, which have previously shown correlations between c-axis length (or unit cell volume) and intermolecular interchain Se–Se distances.[12,13] Therefore, previously suggested correlations between specific crystallographic parameters and *inter*chain Se–Se distances (d_6–d_8 in Figure 2) in (TMTSF)$_2$X derivatives must be viewed with caution unless a series of anions of varying size, but of the same symmetry, have been investigated.[14] Obviously, crystal-packing effects are very important in these salts, and it is likely that only detailed calculations will reveal if these somewhat random changes in interchain Se–Se distances, which occur as a function of temperature, result from electronic or steric factors. Finally, it should be noted that the shortest anion–Se distances (d_9, d_{10}; F--Se) are very similar to those observed in (TMTSF)$_2$X, X = ClO$_4^-$ and PF$_6^-$, at 300 and 125 K but are ~0.15 Å longer than the shortest Se--O distance (3.01 Å) found when X = ReO$_4^-$.[7] It is believed that this short Se--O separation results in the ordering of the ReO$_4^-$ ions in (TMTSF)$_2$ReO$_4$ due to the interaction of electrons of the ReO$_4^-$ anions with TMTSF conduction electrons. A similar mechanism could, of course, operate in (TMTSF)$_2$H$_2$F$_3$.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under Contract W-31-109-Eng-38. The support of NATO (Grant No. 016.81), which has made collaboration between foreign scientists possible, is also gratefully acknowledged.

Supplementary Material Available: Tables of final positional parameters, final temperature factors, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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[13] Flandrois, S.; Coulon, C.; Delhaes, P.; Chasseau, D.; Hauw, C.; Gaultier, J.; Fabre, J. M.; Giral, L. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 307.

[14] It should be noted that the *intra*chain stacking separations (D_1 and D_2 in Figure 2) do decrease in a qualitative manner with unit cell volume and the lowest values known are those for (TMTSF)$_2$H$_2$F$_3$. In spite of this finding, (TMTSF)$_2$H$_2$F$_3$ does not have the highest a-axis electrical conductivity observed in a TMTSF derivative.

Additions and Corrections

1982, Volume 21

D. Attanasio,* C. Bellitto,* A. Flamini,* and G. Pennesi: EPR Spectra of Eight-Coordinated Complexes of the Early Transition Metals with Sulfur and Selenium Donor Ligands. 3. Vanadium(IV) and Niobium(IV) Dithio- and Diselenocarbamates.

Page 1462. The two formulas (C$_2$H$_5$)CS$_2^-$Na$^+$ and (C$_2$H$_5$)CSe$_2$H in the Reagents section should be read: (C$_2$H$_5$)$_2$NCS$_2^-$Na$^+$ and (C$_2$H$_5$)$_2$NCSe$_2$H.—D. Attanasio