

Two Tetrathiafulvalene Salts of a New Thiophene-functionalised Ferracarborane: Electrical Conductivity as a Function of Crystal Composition

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Two tetrathiafulvalenium (TTF) salts of the new sandwich complex *commo*-[3,3'-Fe{1-(thiophene-2-yl)-1,2-C₂B₉H₁₀}₂]⁻, [TTF][Fe(C₂B₉H₁₀C₄H₃S)₂] **2** and [TTF]₅[Fe(C₂B₉H₁₀C₄H₃S)₂]₂ **3**, are synthesized; while the 1:1 salt is an insulator, the 5:2 salt is a semiconductor featuring a conducting superlattice associated with a sublattice that shows ferromagnetic interactions between the ferracarborane complexes; single crystal X-ray studies of the 5:2 salt indicate that the electrical conductivity originates from a unique mixed-valence TTF network.

There is considerable current interest in charge-transfer salts of generic derivatives of tetrathiafulvalene (TTF), many of which exhibit interesting structural and conductivity properties.¹ For example, the recently reported metallacarborane salts [TTF]⁺[M(C₂B₉H₁₁)₂]⁻ (M = Cr, Fe, Ni)² show significant variations in conductive properties as the number of d electrons is changed—the chromacarborane salt being a semiconductor ($\sigma_{RT} = 3 \times 10^{-4} \text{ S cm}^{-1}$) with an activation energy of 0.16 eV while the nickelacarborane salt is an insulator. We now report that the introduction of thiophene substituents on the metallacarborane anion encourages the propagation of mixed-valence TTF stacks. The new ferracarborane *commo*-[3,3'-Fe{1-(thiophene-2-yl)-1,2-C₂B₉H₁₀}₂]⁻ **1** has pendant thiophene groups and its TTF salts [TTF][Fe(C₂B₉H₁₀C₄H₃S)₂] **2** and [TTF]₅[Fe(C₂B₉H₁₀C₄H₃S)₂]₂ **3** exhibit interesting structural and physical property differences.³

Reaction of [TTF]⁺Cl⁻ with the sodium salt of **1** in aqueous solution resulted in the formation of **2**, and black needles of 2·C₇H₈ were obtained by layering an acetone–dichloromethane (*ca.* 1:1 *v/v*) solution of **2** with toluene at *ca.* -20 °C. However, a recrystallization by slow evaporation of an acetone–ethanol (*ca.* 1:1 *v/v*) solution of **2** resulted in the recovery of black plates of the mixed valence salt **3**. The conversion of the simple [TTF]⁺ salt into the mixed valence salt under such mild conditions is unique; it appears that reduction of [TTF]⁺ units in **2** by ethanol is the most probable source of neutral/partially oxidised TTF molecules in **3**. The presence of mixed oxidation states for the TTF units in **3** is consistent with the presence of a charge-transfer absorption band at *ca.* 4120 cm⁻¹ in its IR spectrum,[†] and with its semiconducting nature.

Electrical conductivities of crystalline samples of 2·C₇H₈ ($\sigma_{290\text{K}} \leq 10^{-7} \text{ S cm}^{-1}$) and **3** ($\sigma_{300\text{K}} 2 \times 10^{-3} \text{ S cm}^{-1}$, activation energy 0.22 eV) indicate that these materials are, respectively, an insulator and a semiconductor. Between 25 and 295 K, the corrected molar magnetic susceptibilities of 2·C₇H₈ and **3** follow the Curie–Weiss Law, $\chi = C/(T - \theta)$, with θ values of 0.5 and 1.9 K, respectively. The θ values indicate that weak ferromagnetic interactions between the unpaired spins of the ferracarborane ions exist in both materials. The $\sqrt{8C}$ values of 2.0 and 3.0 μ_B for 2·C₇H₈ and **3**, respectively, are consistent with zero spin contribution from the TTF units to the bulk susceptibilities.

The X-ray structure of 2·C₇H₈ shows the [TTF]⁺ cations form centrosymmetric stacked dimers with TTF units in each dimer being virtually eclipsed at an interplanar separation of 3.45 Å. Each dimer is effectively isolated from other dimers by surrounding anions and toluene solvate molecules which thus disrupt the formation of extended TTF stacks suitable for electrical conduction.

The X-ray structure of **3** features an asymmetric unit containing one ferracarborane anion, one whole TTF unit and three half TTF units so that the unit cell of the compound

contains four independent TTF molecules. In contrast to 2·C₇H₈, the crystal lattice of **3** (Fig. 1) features extended columns of centrosymmetric stacked trimers of TTF units which propagate along the *a* axis. The interplanar separation between TTF units within a trimer is 3.47 Å, whilst that between adjacent trimers is 3.54 Å and the inter-trimer S...S distances (3.90–3.98 Å) are longer than the intra-trimer S...S contacts (3.45–3.54 Å). A centrosymmetric TTF unit lies approximately orthogonal to the TTF units in the trimers and links adjacent columns *via* short S...S contacts of 3.56 Å, giving an unprecedented continuous two-dimensional layer of linked TTF trimers. The 'orthogonal' S...S linkage of TTF units also features in the packing of [TTF]₃[Pt(S₂C₂O₂)₂] and [TTF]₂[Ni(S₂C₂H₂)₂], leading in each case to ribbons of stacked TTF dimers.^{4,5} Notably, in the nickel(II) crystal electrical conductivity along the bridging direction was established, indicating an appreciable interaction between the dimers and the bridging TTF units.⁵ The remaining TTF unit in the unit cell of **3** is involved in S...S bonding interactions with the thiophene-2-yl groups of two adjacent ferracarborane anions related by an inversion centre. Thus the TTF-linked anion pairs propagate along the *a* axis to form

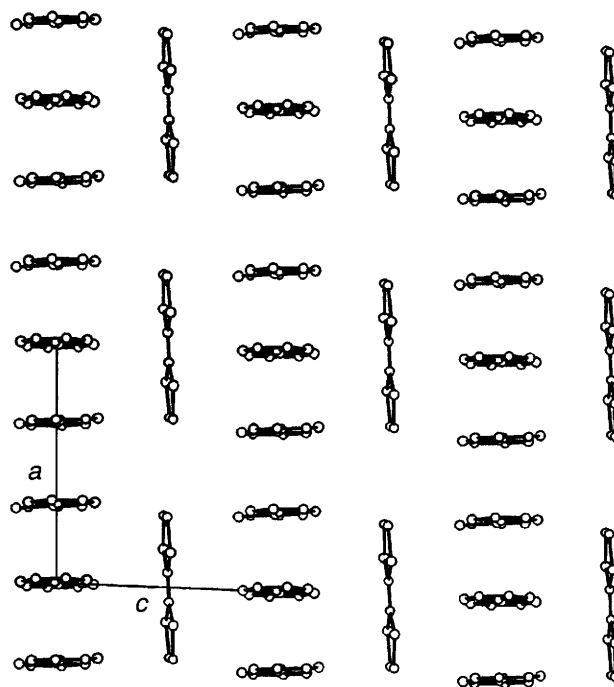


Fig. 1 The two-dimensional sheet of interacting TTF molecules in the crystal lattice of [TTF]₅[Fe(C₂B₉H₁₀C₄H₃S)₂]₂ **3** viewed down the *b* axis

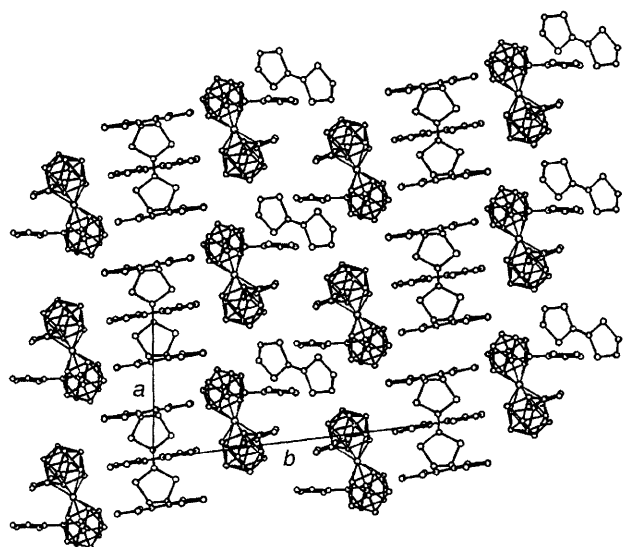


Fig. 2 The crystal packing of $[\text{TTF}]_5[\text{Fe}(\text{C}_2\text{B}_9\text{H}_{10}\text{C}_4\text{H}_3\text{S})_2]_2$ **3** viewed down the c axis and along the sheets of interacting TTF molecules, showing the layers of linked ferracarborane anions and TTF units separating the sheets

continuous 'ribbons' alternating with the TTF sheets (Fig. 2). Variations in length for corresponding bonds in the different types of TTF unit in **3** are consistent with the mixed valence formulation of the material.

The coexistence in **3** of a conducting superlattice with a sublattice which shows ferromagnetic interactions is interesting and merits further investigation.

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Footnotes

† The IR spectrum of **3** is dominated by an intense, broad charge-transfer band which peaks at *ca.* 4120 cm^{-1} and tails off at *ca.* 1410 cm^{-1} . This electronic band (band A in the notation of Torrance *et al.*)⁶ is characteristic of a mixed-valence state in TTF-type donor molecules. The C–H and B–H stretching absorptions are superimposed on the low energy side of the charge-transfer band. The $a_g(\nu_3)$ band of **3** occurs between 1400 and 1100 cm^{-1} as a very strong and broad band with its maximum at 1315 cm^{-1} . The $a_g(\nu_6)$ band occurs at 444 cm^{-1} and is also very strong and broad. The corresponding bands in **2** occur at 1357 and 492 cm^{-1} . The unusually high intensity and low frequency of the vibronic bands of **3** may indicate that the TTF a_g vibrational modes are strongly coupled to the inter-TTF charge-transfer transitions. The breadth of the $a_g(\nu_3)$ band and the presence of shoulder peaks cannot be explained solely by the presence of neutral TTF molecules in the crystal lattice of **3** as TTF itself does not absorb strongly in this spectral region.⁷ A more likely explanation is that the three different types of TTF shown to be in close proximity by X-ray studies facilitate intermolecular charge transfer and vibronic intensity enhancement of the $a_g(\nu_3)$ modes of all three types of TTF. Different $a_g(\nu_3)$ absorption frequencies are expected for each type of TTF as they have different charges.⁸ Correspondingly, the charge transfer band A presents two broad

shoulder peaks on the near-IR side, at 5235 and 6175 cm^{-1} , respectively, indicating the occurrence of more than one charge-transfer transition among the three types of TTF.

‡ *Crystal data for 2-C₇H₈: C₂₅H₃₈B₁₈FeS₆, $M = 781.3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.198(2)$, $b = 32.301(5)$, $c = 12.160(3)\text{ \AA}$, $\beta = 109.51(2)^\circ$, $U = 3775.6(18)\text{ \AA}^3$, $Z = 4$, $D_c = 1.375\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 7.3\text{ cm}^{-1}$, $F(000) = 1600$, crystal size $0.31 \times 0.21 \times 0.10\text{ mm}$. 1403 Independent intensity data with $I/\sigma(I) > 3$ were collected on a Philips PW1100 diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71069\text{ \AA}$) and a θ - 2θ scan mode ($3 \leq \theta \leq 21^\circ$). The structure was solved by the Patterson method.⁹ H atoms of the $[\text{TTF}]^+$ cations and the toluene solvate molecule were included in idealised positions. An empirical absorption correction¹⁰ was applied (max. 1.037, min. 0.948). Individual weights of $1/\sigma^2(F)$ used and in the final cycles of full-matrix least-squares refinement, anisotropic thermal parameters were assigned to the Fe and S atoms. Refinement converged at $R = 0.0829$ and $R_w = 0.0800$ for 225 parameters.*

§ *Crystal data for 3: C₅₄H₇₂B₃₆Fe₂S₂₄, $M = 1991.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.666(3)$, $b = 21.429(6)$, $c = 9.884(3)\text{ \AA}$, $\alpha = 102.81(5)$, $\beta = 93.76(4)$, $\gamma = 82.01(4)^\circ$, $U = 2180.0(16)\text{ \AA}^3$, $Z = 1$, $D_c = 1.517\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 9.1\text{ cm}^{-1}$, $F(000) = 1012$, crystal size $0.48 \times 0.40 \times 0.02\text{ mm}$. 3127 Independent intensity data with $I/\sigma(I) > 3$ were collected on a Philips PW1100 diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71069\text{ \AA}$) and a θ - 2θ scan mode ($3 \leq \theta \leq 25^\circ$). The positions of all non-H atoms were obtained by direct methods.⁹ All H atoms were included in structure factor calculations at observed positions with fixed isotropic thermal parameters of 0.08 \AA^2 but their positions were not refined. An empirical absorption correction¹⁰ was applied (max 1.066, min 0.798). Individual weights of $1/\sigma^2(F)$ were assigned to each reflection and in the final cycles of full-matrix least-squares refinement, the Fe and S atoms were given anisotropic thermal parameters. Refinement converged at $R = 0.0575$ and $R_w = 0.0568$ for 299 parameters.*

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors (including Fullerenes): Synthesis, Structure, Properties and Theory*, Prentice-Hall, Englewood Cliffs, NJ, 1992; J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz and M.-H. Whangbo, *Prog. Inorg. Chem.*, 1987, **35**, 51; M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355; D. Jérôme, *Synth. Met.*, 1987, **19**, 1017; J. Stevens, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky, C. W. Rees and O. Meth-Cohn, Pergamon, Oxford, 1984, vol. 1, ch. 1.13, pp. 347–359; A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 1974, **7**, 232; J. B. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79; J. M. Williams, *Prog. Inorg. Chem.*, 1985, **33**, 183; F. Wudl, *Acc. Chem. Res.*, 1984, **17**, 227.
- J. M. Forward, D. M. P. Mingos, T. E. Müller, D. J. Williams and Y.-K. Yan, *J. Organomet. Chem.*, 1994, **467**, 207, and unpublished results.
- Y.-K. Yan, D. M. P. Mingos, M. Kurmoo, W.-S. Li, I. J. Scowen, M. McPartlin, A. T. Coomber and R. H. Friend, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
- C. Bellitto, M. Bonamico, V. Fares, P. Imperatori and S. Patrizio, *J. Chem. Soc., Dalton Trans.*, 1989, 719.
- J. S. Kasper, L. V. Interrante and C. A. Secaur, *J. Am. Chem. Soc.*, 1975, **97**, 890.
- J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman and P. E. Seiden, *Phys. Rev. B*, 1979, **19**, 730.
- R. Bozio, I. Zanon, A. Girlando and C. Pecile, *J. Chem. Phys.*, 1979, **71**, 2282.
- V. M. Yartsev, *Phys. Status Solidi, Sect. B*, 1984, **126**, 501.
- G. M. Sheldrick, *SHELX76*, University of Cambridge, 1976; *SHELX86*, University of Göttingen, 1986.
- N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.