Anion polarity-induced dual oxidation states in a dual-layered purely-organic paramagnetic charge-transfer salt, (TTF)₃(PO-CON(CH₃)C₂H₄SO₃)₂, where PO = 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl Free Radical

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KEYWORDS: tetrathiafulvalene (TTF), organic conductors, organic magnetic materials, organic free radical

Over the past five years numerous organic conductors have been prepared.¹ In particular many researchers have prepared salts of, TTF (tetrathiafulvalene), TMTSF (tetramethyl-tetraselenafulvalene), BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) and derivatives of these electron donors.² This is because the D_mX_n-type charge-transfer (CT) salts (where D = donor, X = anion, and *m*, *n* = 1,2,3...) have a wide variety of ground states ranging from insulating through semiconducting to metallic and superconducting. The donors usually form quasi-1D or 2D conducting layers, which are separated by anions. Usually the anions play no significant role in the conducting properties and prevent donors from approaching one other. Indeed, a salt with smaller anions is often more conductive than an isomorphous salt with larger anions. Therefore, simple and small inorganic anions have been widely used.

We have focused on preparing new organic magnetic anions that are organic free radicals with a sulfonate group (-SO₃⁻).³⁻⁵ The aim is to obtain strong interactions between the conducting and magnetic electrons. However these organic anions are much larger than the commonly used inorganic anions. In fact, most of the resultant TTF, TMTSF, and BEDT-TTF salts are semiconducting.³ Previously we reported a purely organic magnetic conductor using the anion PROXYL-CONHCH₂SO₃⁻. The salt β''-(BEDT-TTF)₂(PROXYL-CONHCH₂SO₃), shows metallic behavior down to 210 K.⁴ We also recently reported the salt κ-β''-(BEDT-TTF)₂(PO-CONHC₂H₄SO₃), which shows metallic behavior down to at least 1.7 K.⁵ The latter salt has two crystallographically independent donor layers, with κ- and β''-arrangements each with a different band filling of 0.8 and 0.7, respectively. Several other salts that have two different packing arrangements for donor layers have been reported.^{5,6} For example, α-β''-(BEDT-TTF)₄[(NH₄)M(C₂O₄)₃](solvent),^{6g} for which the authors stated the dual-layered structure was caused by the anisotropy of the anion layer, two sides of which are not equivalent. Furthermore, Schlueter *et al.* recently reported a new superconductor, κ-α''-(BEDT-TTF)₂Ag(CF₃)₄(1,1,2-trichloroethane).^{6k} The authors stressed that this molecule-based superconductor with dual BEDT-TTF packing motifs has a *T_C* five times higher than that of its polymorph which contains only κ-type packing. In this communication, we introduce a new magnetic anion PO-CON(CH₃)C₂H₄SO₃⁻. We also describe the structure and physical properties of a dual-layered TTF salt of this anion.

The acidic sulfonate (**1**) was prepared by reacting 3-carboxy-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl (PO-COOH, 0.50 g, 2.7 mmol) with 2-methyltaurine (H₃CNHCH₂CH₂SO₃H, 0.38 g, 2.7 mmol) in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC, 0.67 g, 3.3 mmol) and 4-dimethylaminopyridine (DMAP, 0.80 g, 2.7 mmol) in 20 mL of CH₂Cl₂ at ambient temperature with stirring over a week. Metathesis of H**1** with PPh₄Br yielded the PPh₄ salt of **1** as yellow crystals (**2**), which were then recrystallized from acetone (yield 29 %). X-ray diffraction data of **2** were collected, at ambient temperature, using a Rigaku AFC-7R diffractometer equipped with an ADSC Quantum1 CCD area detector. The structure was assigned as PPh₄·**1**·H₂O.⁷ The asymmetric unit contains one PPh₄ cation, one anion, and one water molecule. A N-O distance in the PO radical of 1.269(5) Å was observed. There are two crystallographically independent hydrogen bonds between the water molecule and the sulfonate group of **2** (O...O = 2.800(3) and 2.813(5) Å). The hydrogen bonding means that each anion **2** forms a dimer (Figure S1 in the Supporting Information). The magnetic susceptibility of a polycrystalline sample from 2-300 K using a Quantum Design MPMS-5S SQUID magnetometer obeys a Curie-Weiss law with *C* (Curie constant) = 0.356 emu K/mol and *θ* (Weiss temperature) = -0.10 K.

Metathesis of **2** (14.0 mg) with (TTF)₃(BF₄)₂ (17.3 mg) in 40 mL of acetonitrile gave black elongated plates (**3**). Single crystal X-ray diffraction data were collected with the same CCD system as used for **2**, at 293 K. The resultant data were solved as (TTF)₃(**1**)₂.⁸ The crystal structure of **3** is shown in Figure 1. The asymmetric unit has one type of TTF (TTF-A) and a half of a TTF-B donor and one anion **1**. In the unit cell, there are two crystallographically independent donor sheets, which consist of either TTF-A or TTF-B, respectively. Figure 1b shows the packing within the TTF-A donor sheet. Each TTF-A exists in a dimer, which stack along the *c*-axis with a 31.5° tilt angle. There are four intradimer short S...S contacts and only one interdimer S...S contact. The dimers also interact along the side-by-side direction (*//* to *b*) with many short S...S contacts to form a 2D conducting sheet. Figure 1c shows the structure of the TTF-B donor sheet along the direction normal to the TTF-B molecular plane. Three short S...S contacts were observed along the side-by-side direction, suggesting a strong interaction along the *b*-axis. On the other hand, little face-to-face interaction was observed along the *a*-axis (see also Figure 1a). This suggests that the TTF-B sheet has a quasi-1-D electronic structure along the side-by-side direction. In addition, the spin center N-O bond distance in the anion is 1.270(6) Å, which is not significantly different from that observed in the PPh₄ salt **2**.

Surprisingly, in the anion layer, all anions are oriented in the same direction to form a head-to-head uniform arrangement (Figure 1a). The spin center N-O $\cdot$ group is always oriented to face a TTF-B molecule with a short S $\cdots$ O contact of 3.261(4) Å. Since TTF-B is about the center of symmetry, both spin centers interact with each other via a TTF-B (Figure 1d). The effect on the magnetic properties will be discussed later. On the other hand the sulfonate group, located at the opposite end of the anion, is oriented to face the TTF-A molecule. There are two short S $\cdots$ O contacts (3.005(4) and 3.254(4) Å) between -SO $_3^-$ and TTF-A (Figure 1e). The anisotropy of the anionic layer along the *a*-axis gives the structure a dual donor layer motif and a polar anionic layer. The short contacts between TTF-A and -SO $_3^-$ presents a more negative dipole field to the TTF-A layers than to the TTF-B layers. We estimate the charge on each TTF, using bond distances, of +0.86 and +0.51 for TTF-A and TTF-B, respectively.⁹ The charges, normalized by the total number of holes in the asymmetric unit, are +0.77 and +0.46 for TTF-A and B, respectively. This indicates that TTF-A is more positive than TTF-B, which makes sense with respect to the dipole moment of the anion layer, namely the more positive TTF-A layers lie close to more negative -SO $_3^-$ group. A similar charge difference was observed in κ - β'' -(BEDT-TTF) $_2$ (PO-CONHC $_2$ H $_4$ SO $_3$)⁵ in which a more positive β'' -layer lies close to the sulfonate groups, whereas a less positive κ -layer faces the N-O $\cdot$ groups, although we did not previously mention why the charges of both layers are different.⁵ The similarity of the present and previous compounds and a recent report by H. Yamochi et al. has strengthened our current hypothesis. Yamochi. reported the molecular alloy, [(EDO-TTF) $_{1-x}$ (MeEDO-TTF) $_x$] $_2$ PF $_6$.¹⁰ If *x* is small the charge disproportionation was observed in which the donors close to the anions have the molecular charge of +1 and the other TTF derivatives are neutral. On the other hand, if *x* is large (as inferred, by the authors, from an increased donor $\cdots$ anion distance since the molecular size of MeEDO-TTF is larger than EDO-TTF), the charge is distributed equally over the donor layer. The result suggests that a change in the donor $\cdots$ anion distance leads to the change in the donor charge. For a small *x*, the anion layer is studded with negative charges, therefore the adjacent donor layer is studded with neutral and monovalent donors. For the compound presented here, the negative charges of the anion layer are localized on one side of the layer, which induces the adjacent donor (TTF-A) layer to become more positive and so the other donor layer is less positive. This is the first case in which an anisotropic arrangement of the anion layer provides not only the dual structure but also the different oxidation states of the dual donor layers. The situation is schematically shown at the left side in Figure 3. In addition, the net dipole moment of the crystal is zero as a consequence of the centrosymmetric space group, C2/c.

The magnetic susceptibility of a powdered sample of **3** from 2–300 K was measured using a Quantum Design MPMS-5H SQUID magnetometer. Figure 2 shows χT -*T* plots for the salt **3**. The data can be modeled by Curie-Weiss law with *C* = 1.098 emu K/mol and θ = -5.5 K. The *C* value per (TTF) $_3$ (**1**) $_2$ is 293 % of that for an *s* = 1/2 spin (0.375 emu K/mol). This suggests that (TTF) $_3$ (**1**) $_2$ has approximately three spins. Each radical anion **1** has one spin so the rest is located in both or one of the TTF layers. In other words the TTF-A and/or TTF-B layers display magnetically localized insulating states.

Temperature-dependent electrical resistivity of the salt **3** was measured by the conventional four-probe method. The salt is a semiconductor with ρ_{RT} = 230 Ω ·cm and *E*_a = 0.10 eV. This and the magnetic result suggest that both donor layers are in a Mott insulating and/or a charge disproportionate states.

Figure 1. (a) Crystal structure of **3**. (b) Packing motif of the TTF-A layer. (c) Packing motif of the TTF-B layer. Dashed lines indicates S $\cdots$ S short contacts less than the van der Waals distance of 3.70 Å. (d) Molecular structure of TTF-B and the anions with short S $\cdots$ O contacts. (e) Molecular structure of TTF-A and the anion **1** with the short S $\cdots$ O contacts.

Figure 2. χT -*T* plots for salt **3** where χ is the molar magnetic susceptibility per (TTF) $_3$ (**1**) $_2$.

As previously mentioned, the molecular charges of TTF-A and TTF-B are +0.77 and +0.46, respectively. The band fillings (*BF*) are therefore 0.62 and 0.77 for the TTF-A and TTF-B layers, respectively, which are close to 5/8 and 3/4. Also the TTF-A layer has a parallel face-to-face dimer, which stacks along the *c*-axis with a tilt angle (Figure 1b). This indicates four-fold structure along the stacking direction. If the charge of TTF-A is +0.75 (*BF* = 5/8), one electron (= three holes) is located on the each tetramer. Therefore, the TTF-A sheet is likely to be a Mott insulator. This suggests that there is one spin on the tetramer so that (TTF-A) $_2$ has a half spin. The other half spin is therefore located on the TTF-B layer. As shown in Figure 1c, TTF-B forms a 1D uniform chain in the side-by-side direction. If the layer is quarter filled (*BF* = 3/4), the layer should become a metal, which contradicts the resistivity measurements. Although we have not yet observed

any satellite spots or diffuse streaks on any X-ray photos at room temperature, we speculate that TTF-B forms a dimer or the layer is in a 0101 charge disproportionate state to have one spin per two TTF molecules. Extra spots or streaks may be observed at lower temperature. The situation is schematically shown at the right side in Figure 3.

Figure 3. Schematic scheme of the electronic (left) and magnetic (right) structure of **3**.

The relatively large θ of -5.5 K indicates that there is an anti-ferromagnetic interaction between the spins. As shown in Figure 1d, the spins on the anions interact with each other via the TTF-B molecule. However magnetic interactions mediated by TTF molecules are usually very weak ($\ll 1$ K)^{3c,d} compared to when the localized spins are in the same donor layer. The observed susceptibility (χ_{Total}) is a summation of the susceptibility contributed by the three spins [$\chi_{\text{Total}} = \chi_{\text{PO}} + \chi_{\text{TTF-A}} + \chi_{\text{TTF-B}} = C_{\text{PO}}/(T - \theta_{\text{PO}}) + C_{\text{TTF-A}}/(T - \theta_{\text{TTF-A}}) + C_{\text{TTF-B}}/(T - \theta_{\text{TTF-B}})$]. We may make some assumptions: the spin concentration ($\approx$ purity) is the same for all spins (thus, $2C_{\text{PO}} = 0.5C_{\text{TTF-A}} = 0.5C_{\text{TTF-B}}$); the spin-spin interaction between the PO radicals is zero ($\theta_{\text{PO}} = 0.0$); the magnetic interaction in the TTF-A layer is approximately as strong as that in the TTF-B layer ($\theta_{\text{TTF-A}} = \theta_{\text{TTF-B}}$). With this in mind we remodelled the magnetic curve, which yielded a θ value ($= \theta_{\text{TTF-A}} = \theta_{\text{TTF-B}}$) of -19.1 K. Further experiments are now in progress.

In conclusion, in the CT salt (TTF)₃(**1**)₂ the anisotropic anion **1** forms a head to head arrangement in the anionic layer, which not only gives dual donor layers but also leads to a dipole electric field, which provides different oxidation states for each donor layer. The three localised spins are located on the free radical of the anion **1** and also on both TTF sheets.

Supporting Information Available: Additional information and figures (PDF); crystallographic information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Crystal data for **2**: PPh₄**1**·H₂O, C₃₆H₄₂N₂O₆PS, M = 661.77, Triclinic $P\bar{1}$, $a = 11.3326(14)$, $b = 12.7665(12)$, $c = 13.3078(12)$ Å, $\alpha = 93.603(6)^\circ$, $\beta = 113.6220(10)^\circ$, $\gamma = 91.911(2)^\circ$, $V = 1756.9(4)$ Å³, $Z = 2$, $D_c = 1.251$ g cm⁻³, $\text{MoK}\alpha$, $\lambda = 0.71073$ Å, $\theta_{\text{max}} = 27.5^\circ$, $T = 295$ K, total data 15512, unique data 7381, $\mu = 0.1839$ mm⁻¹, 458 parameters, $R = 0.068$, $R_w = 0.069$ on $|F|$ and $S = 1.092$. (See Supporting Information for further details).
- (8) Crystal data for **3**: (TTF)₃(**1**)₂, C₄₂H₅₂N₄O₁₀S₁₄, M = 1221.73, Monoclinic C2/c, $a = 59.415(4)$, $b = 6.3283(3)$, $c = 14.9010(7)$ Å, $\beta = 102.2424(14)^\circ$, $V = 5475.3(6)$ Å³, $Z = 4$, $D_c = 1.482$ g cm⁻³, $\text{MoK}\alpha$, $\lambda = 0.71073$ Å, $\theta_{\text{max}} = 27.5^\circ$, $T = 293$ K, total data 21998, unique data 5827, $\mu = 0.611$ mm⁻¹, 342 parameters, $R = 0.065$, $R_w = 0.059$ on $|F|$ and $S = 1.204$. (See Supporting Information for further details).
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SYNOPSIS TOC The purely organic paramagnetic charge-transfer salt, $(\text{TTF})_3(\text{PO-CON}(\text{CH}_3)\text{C}_2\text{H}_4\text{SO}_3)_2$ was prepared. The anisotropic anion forms a head-to-head arrangement in the anionic layer, giving dual donor layers with different oxidation states. SQUID magnetometry indicates that spins are localized not only on the free radical (PO) but also on both TTF layers.