

## A Purely Organic Paramagnetic Metal, $\kappa$ - $\beta''$ -(BEDT-TTF)<sub>2</sub>(PO-CONHC<sub>2</sub>H<sub>4</sub>SO<sub>3</sub>), Where PO = 2,2,5,5-Tetramethyl-3-pyrrolin-1-oxyl Free Radical<sup>†</sup>

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Organic conducting salts, based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), have been prepared with a wide variety of counteranions.<sup>1</sup> The transport properties range from insulating through semiconducting to metallic and superconducting and are dependent in part on the packing of the BEDT-TTF molecules. The packing motifs have been classified into several types designated by the labels  $\alpha$ ,  $\beta$ ,  $\beta''$ ,  $\kappa$ ,  $\lambda$ ,  $\theta$ , etc.<sup>1,2</sup> Evidently, the donor arrangements play a crucial role in determining the transport properties, because  $\kappa$ - and  $\beta$ -type salts usually have metallic properties,  $\alpha$ -type salts are usually semiconductors,  $\beta''$ -type salts are weak metals or semimetals, and so on.

After the discovery of the BEDT-TTF-based paramagnetic superconductor,  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]. PhCN,<sup>3</sup> charge-transfer (CT) salts with transition metal anions have attracted great interest.<sup>4</sup> In particular, the  $\lambda$ -(BETS)<sub>2</sub>FeCl<sub>4</sub> family have unique electromagnetic properties that emerge from an interaction between localized and itinerant electrons.<sup>5</sup> However, the interaction is small (<10 K), probably because there is no direct overlap between the p $\pi$  orbitals of the donor molecule and the d orbitals of the transition metal. To make CT salts that have larger interactions, one strategy has been to use a different source of unpaired electron density, organic free radicals, which can directly overlap with the donor p $\pi$ orbitals. To this end, many researchers have tried intro-

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ducing aminoxyl radicals ( $R_2NO \cdot$ ), but as of yet, no other group has prepared a metallic salt.<sup>6</sup> Similarly, we prepared five BEDT-TTF salts containing the TEMPO radical (see scheme) and all are semiconductors.7a-e We then reported the first metallic salt (albeit only down to 210 K) containing the smaller PROXYL radical,  $\beta''$ -(BEDT-TTF)<sub>2</sub>(PROXYL-NHCOCH<sub>2</sub>SO<sub>3</sub>).<sup>7f</sup> We then prepared an anion with the even smaller PO (2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl) radical, PO-NHCOCH<sub>2</sub>SO<sub>3</sub> $^{-}$ (1), but the resultant BEDT-TTF salt had an  $\alpha$ -type packing motif and was a semiconductor.<sup>7g</sup> In this communication, we report the larger anion PO-NHCOCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub> $^{-}$  (2) which includes the same PO radical but with the longer ethylene group instead of the methylene group of anion 1. This new anion 2 has provided a BEDT-TTF salt, the structure and properties of which are reported.



The sulfonic acid H2 was prepared by reacting 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-oxyl (PO–COOH, 100 mg, 0.54 mmol) with 2-aminoethanesulfonic acid (H<sub>2</sub>NCH<sub>2</sub>-CH<sub>2</sub>SO<sub>3</sub>H, 70 mg, 0.65 mmol) in the presence of DCC (H<sub>11</sub>C<sub>6</sub>–N=C=N–C<sub>6</sub>H<sub>11</sub>, 150 mg, 0.65 mmol) and DMAP (4-(CH<sub>3</sub>)<sub>2</sub>N-pyridine, 180 mg, 1.30 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature with stirring over three days. Metathesis with PPh<sub>4</sub>Br gave PPh<sub>4</sub>**2** as yellow crystals, which were recrystallized from acetone (yield 45%). Single-crystal X-ray diffraction data for PPh<sub>4</sub>**2** were collected using a Quantum CCD area detector and a Rigaku AFC-7R diffractometer.<sup>8</sup> The asymmetric unit contains one PPh<sub>4</sub> cation

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**Figure 1.** (a) Crystal structure of **3**. (b) Packing arrangements of donors in the  $\kappa$ -layer and (c) the  $\beta''$ -layer. Dashed lines indicate  $S \cdots S$  contacts shorter than the sum of the van der Waals radii (<3.70 Å). (d) Packing arrangement of the anion layer. (e) Molecular structure of the  $\kappa$ -layer donors and the anions showing the short  $S \cdots O$  contact.

and one anion. The magnetic susceptibility of a polycrystalline sample of PPh<sub>4</sub>**2** was measured using a Quantum Design MPMS-5S SQUID magnetometer. The data can be modeled by a Curie–Weiss law with C = 0.370 emu K/mol and  $\theta = -0.39$  K.

Black needlelike crystals of  $\kappa$ - $\beta''$ -(BEDT-TTF)<sub>2</sub>(PO-CONHC<sub>2</sub>H<sub>4</sub>SO<sub>3</sub>), **3**, were obtained by the conventional constant-current electrocrystallization method in a mixed solvent of PhCl (18 mL) and CH<sub>3</sub>CN (2 mL) with 15 mg of BEDT-TTF and 70 mg of PPh<sub>4</sub>**2**. X-ray diffraction data were recorded at 293 K with the same CCD system as used for PPh<sub>4</sub>**2**.<sup>9</sup> The crystal structure of **3** is shown in Figure 1a. In the asymmetric unit there are four BEDT-TTF molecules and two anions. Therefore, the formula charge of BEDT-TTF is +0.5 and the formula band filling is

- (8) Crystal data for PPh<sub>4</sub>**2**:  $C_{35}H_{38}N_2O_5PS$ , M = 629.73, triclinic  $P\overline{I}$ , a = 11.6417(6) Å, b = 11.7774(7) Å, c = 13.7069(13) Å,  $\alpha = 112.458(3)^\circ$ ,  $\beta = 99.9654(9^\circ)$ ,  $\gamma = 99.1630(10)^\circ$ , V = 1657.4(2) Å<sup>3</sup>, Z = 2,  $D_c = 1.262$  g cm<sup>-3</sup>, MoK<sub>a</sub>,  $\lambda = 0.71073$  Å,  $\theta_{max} = 27.5^\circ$ , T = 295 K, total data 14488, unique data 6879,  $\mu = 0.1893$  mm<sup>-1</sup>, 435 parameters, R = 0.070,  $R_w = 0.057$  on |F|, and S = 1.094 (see the Supporting Information for further details).
- (9) Crystal data for 3: C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>O<sub>5</sub>S<sub>17</sub>, M = 1059.74, triclinic  $P\overline{1}$ , a = 8.711(2) Å, b = 11.8136(4) Å, c = 40.528(7) Å,  $\alpha = 89.448(2)^{\circ}$ ,  $\beta = 87.3821(12)^{\circ}$ ,  $\gamma = 83.2487(9)^{\circ}$ , V = 4137.3(12) Å<sup>3</sup>, Z = 4,  $D_c = 1.70$  gcm<sup>-3</sup>, MoK<sub> $\alpha$ </sub>,  $\lambda = 0.71073$  Å,  $\theta_{max} = 27.5^{\circ}$ , T = 293 K, total data 27895, unique data 6689,  $\mu = 0.930$  mm<sup>-1</sup>, 989 parameters, R = 0.080,  $R_w = 0.075$  on |F|, and S = 1.151 (see the Supporting Information for further details).
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0.75. The structure consists of alternating donor and anion layers propagated along the crystallographic c axis. There are two crystallographically independent donor layers with  $\kappa$ - and  $\beta''$ -type arrangements shown in panels b and c in Figure 1, respectively.<sup>10</sup> For each donor A-D (Figure 1b,c) we estimate the charge, using bond lengths<sup>12</sup> of +0.17, +0.83, +0.85, and +0.60, respectively. The charges, normalized by the total number of holes in the asymmetric unit, are +0.14, +0.67, +0.70, and +0.49 for A–D, respectively. The band filling for the  $\kappa$ - and  $\beta''$ layers is different at 0.80 and 0.70, respectively.<sup>13</sup> The result suggests that the  $\kappa$ -layer has more electrons than the  $\beta''$ -layer, in order to equalize their Fermi level. The band fillings are slightly different from the formula band filling of 0.75, which may make both the  $\beta''$ - and  $\kappa$ -layer metallic although the  $\kappa$ -layer has considerble charge disproportionation.<sup>14c</sup> In the anionic layers (Figure 1d), the anions are all oriented in the same direction and no short contacts were observed between the spin centers of the PO radicals (the shortest  $O \cdots O$  distance is 5.880(19) Å). Figure 1a shows that the sulfonate groups  $(-SO_3^-)$  are oriented to face the  $\beta''$ -layers and the N–O atoms, which carry the unpaired spin, are oriented to face the  $\kappa$ -layers. The anisotropy of the anionic layers along the *c*-axis appears to lead to the structure having the two crystallographically independent donor layers. In fact, a magnetically important short contact between the anionic spin center O atom and a sulfur atom of the BEDT-TTF molecule in the  $\kappa$ -layer (O5 · · · S1) of 3.638(10) Å is observed (Figure 1e),<sup>15</sup> although it is slightly longer than the sum of the van der Waals radii (3.37 Å). In addition, there are two independent N-O distances for the PO moieties of 1.252(13) Å for N2-O5 and 1.286(14) Å for N4-O10 (Figure 1e). Only the latter is close to the N–O distance in  $PPh_42(1.281(4) \text{ Å})$  and is in the range found for the TEMPO radicals (1.27–1.30 Å).<sup>16</sup> As mentioned, the O5 atom has a short contact with the S1 atom of the donor, suggesting some electron donation from the PO radical to the  $\kappa$ -layer.<sup>17</sup>

The electrical resistivity of the single crystals were measured by a conventional four probe method. At 300 K a resistivity of  $1.6 \times 10^{-2} \Omega$  cm was observed. The temperature dependence of the electrical resistivity is shown in Figure 2a. From 300 K the resistivity decreases gradually with decreasing temperature to 70 K, below which it decreases more rapidly down to 1.7 K. Thus, this is the

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- (15) The shortest S···O contact between the other independent anion 2 and a BEDT-TTF molecule (S15-010, Figure 1e) is 3.989(11) Å.
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**Figure 2.** (a) Temperature-dependent electrical resistivity of **3**. (b) Calculated Fermi surfaces of (I, II)  $\kappa$ - and (III, IV) $\beta''$ -layers at the band filling of (I) 0.80, (II) 0.75, (III) 0.70, and (IV) 0.75, respectively.

first metal containing an aminoxyl radical that is stable to such low temperatures.

The electronic structure has been characterized using extended Hückel tight-binding band structure calculations<sup>19</sup> for each of the different two-dimensional donor sheets. Figure 2b shows Fermi surfaces of the  $\kappa$ - (I, II) and  $\beta''$ -layers (III, IV) at the band filling of 0.80 (I), 0.75 (II), 0.70 (III), and 0.75 (IV), respectively. Despite of the difference in the band filling both Fermi surfaces for the  $\kappa$ - and  $\beta''$ -layers are similar to each other. The band dispersion (Figure S1 in the Supporting Information) of the  $\beta''$ -layer has no significant midgap but that of  $\kappa$ -layer has a mid-gap-like split, suggesting that the  $\kappa$ -layer can become a Mott insulator if the band fillng is 0.75. In addition, the calculation including the charge-ordering effect was also calculated for  $\kappa$ -layer. Fermi surface area decreses with increarsing the charge-ordering effect (Figure S1e in the Supporting Information).

The temperature-dependent magnetic susceptibility of 3 was measured using a Quantum Design SQUID magnetometer from 2 to 300 K (MPMS-5SH) and from 0.5 to 2 K (MPMS-XL5 with an IQUANTUM iHelium3 <sup>3</sup>He refrigerator). The  $\chi$ -T curve (Figure 3a) has a broad maximum around 1 K, below which  $\chi$  decreases with decreasing temperature. We also measured the magnetic susceptibility of a bundle of the needle crystals oriented in four glass capillaries  $(1 \text{ mm}\phi)$  parallel and perpendicular to the crystal long axis (//b), but no anisotropy was observed (Figure S2 in the Supporting Information). The result suggests that the  $\chi$  drop is not caused by an antiferromagnetic transition. In fact, the powder data (Figure 3a) can be modeled by a 1D Heisenberg S = 1/2alternating chain expression<sup>20</sup> with p (spin concentration) =  $0.975, J_1 = -0.80, J_2 = -0.69$  K. The *p* value is close to 1.0, as predicted for the PO radical, suggesting that this moiety dominates the Heisenberg term. To obtain the Pauli paramagnetic contribution from the BETD-TTF layers ( $\chi_{ET}$ ), we subtracted the anionic Heisenberg term from the total data. The resultant curve is shown in Figure 3b (from 2 to 300 K).<sup>21</sup> The value of  $3.5-4.2 \times 10^{-4}$  emu/mol is in the



**Figure 3.** (a) Temperature-dependent magnetic susceptibility  $(\chi - T \text{ plot})$  of the powder sample of **3**. The dashed line is calculated on the basis of an alternate Heisenberg 1D chain model. Inset shows a 1D chain of the anions. (b)  $\chi - T$  plot after subtracting the anionic Heisenberg term from the total magnetic susceptibility (2–300 K). The solid line is a guide to the eyes.

range expected for Pauli paramagnetic susceptibility of organic metals  $(2-6 \times 10^{-4} \text{ emu/mol})$ ,<sup>1</sup> suggesting no charge localization on the donor layers and normal metallic behavior. The small negative J values indicate that there is a short-range weak antiferromagnetic PO···PO interaction. As shown in the inset of Figure 3a, the two independent anions form 1D alternating chains with short N-O···O-N contacts of just less than 6 Å. It is through this 1D network that the PO radicals appear to interact with each other although the intermolecular distances are relatively long. Alternatively the S····O short contact as shown in Figure 1e suggests that the weak antiferromagnetic interaction is mediated by the  $\kappa$ -type donor layers. Because the salt is a metal, it is postulated that the itinerant electrons mediate the antiferromagnetic interaction. However, if this is the case, 2D-like magnetic behavior should be observed, which contradicts with the observed 1D Heisenberg-like result. The confirmation of which route is significant is now in progress.

In conclusion, we have made a novel BEDT-TTF-based purely organic paramagnetic conducting salt that contains the aminoxyl radical. X-ray analysis indicates that there are two crystallographically independent donor sheets with  $\kappa$ - and  $\beta''$ -type structural motifs. The salt is metallic down to 1.7 K, indicating a stable metal. A weak antiferromagnetic interaction between the PO radicals was also observed.

**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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<sup>(21)</sup> Note that there is a deviation of the observed data from the best fitting curve in the low-temperature region (< 50 K, see Figure 3a). Therefore we omitted the  $\chi_{\rm ET}$  values below 2 K in Figure 3a. Such uncertainty in the estimation of  $\chi_{\rm ET}$  at low temperature may indicate that the data does not exactly follow the 1D alternating chain model.