A purely organic paramagnetic metal, $\kappa\text{-}\beta''$ -

(BEDT-TTF)₂(PO-CONHC₂H₄SO₃) where PO =

2,2,5,5-Tetramethyl-3-pyrrolin-1-oxyl free radical

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Organic conducting salts, based on bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), have been prepared with a wide variety of counter-anions.¹ 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 α , β , β'' , κ , λ , θ , etc.^{1,2} Evidently, the donor arrangements play a crucial role in determining the transport properties, since κ - and β -type salts usually have metallic properties, α -type salts are usually semiconductors, β'' -type salts are weak metals or semi-metals, and so on.

After the discovery of the BEDT-TTF-based paramagnetic superconductor, β'' -(BEDT-TTF)₄[(H₃O)Fe(C₂O₄)₃].PhCN,³ charge-transfer (CT) salts with transition metal anions have attracted great interest.⁴ In particular, the λ -(BETS)₂FeCl₄ family have unique electromagnetic properties that emerge from an interaction between localized and itinerant electrons.⁵ However the interaction is small (< 10 K) probably because there is no direct overlap between the π 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 π orbitals. To this end, many researchers have tried introducing aminoxyl radicals (R₂NO·) but, as yet, no other group has prepared a metallic salt.⁶ Similarly, we prepared five BEDT-TTF salts containing the TEMPO radical (see scheme) and all are semiconductors.^{7a-g} We then reported the first metallic salt (albeit only down to 210 K) containing the smaller PROXYL radical, β'' -(BEDT-TTF)₂(PROXYL-NHCOCH₂SO₃).^{7f} We then prepared an anion with the even smaller PO (2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl) radical, PO-NHCOCH₂SO₃⁻ (**1**), but the resultant BEDT-TTF salt had an α -type packing

motif and was a semiconductor.^{7g} In this communication, we report the larger anion PO-NHCOCH₂CH₂SO₃⁻ (**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 H**2** was prepared by reacting 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-oxyl (PO-COOH, 100 mg, 0.54 mmol) with 2-aminoethanesulfonic acid (H₂NCH₂CH₂SO₃H, 70 mg, 0.65 mmol) in the presence of DCC (H₁₁C₆-N=C=N-C₆H₁₁, 150 mg, 0.65 mmol) and DMAP (4-(CH₃)₂N-pyridine, 180 mg, 1.30 mmol) in 30 mL of CH₂Cl₂ at room temperature with stirring over three days. Metathesis with PPh₄Br gave PPh₄**2** as yellow crystals, which were recrystallised from acetone (yield 45%). Single crystal X-ray diffraction data for PPh₄**2** were collected using a Quantum CCD area detector and a Rigaku AFC-7R diffractometer.⁸ The asymmetric unit contains one PPh₄ cation and one anion. The N-O distance in the PO moiety is 1.281(4) Å, which is in the range found for TEMPO radicals (1.27 - 1.30 Å).⁹ The magnetic susceptibility of a polycrystalline sample of PPh₄**2** was measured using a Quantum Design MPMS-5S SQUID magnetometer. The data can be modelled by a Curie-Weiss law with $C = 0.370$ emu·K/mol and $\theta = -0.39$ K.

Figure 1. (a) Crystal structure of **3**. (b) Packing arrangements of donors in the κ -layer and (c) the β'' -layer. Dashed lines indicate S...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 κ -layer donors and the anions showing the short S...O contact.

Black needle-like crystals of κ - β'' -(BEDT-TTF)₂(PO-CONHC₂H₄SO₃), **3**, were obtained by the conventional constant-current electrocrystallisation method in a mixed solvent of PhCl (18 mL) and CH₃CN (2 mL) with 15 mg of BEDT-TTF and 70 mg of PPh₄**2**. X-ray diffraction data were recorded at 293 K with the same CCD system as used for PPh₄**2**.¹⁰ The crystal structure of **3** is shown in Fig. 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 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 κ - and β'' -type arrangements shown in Fig. 1b and 1c, respectively.¹¹ For each donor A to D (Fig. 1b and 1c) we estimate the charge, using bond lengths,¹³ 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 to D, respectively. The band filling for the κ - and β'' -layers is different at 0.80 and 0.70, respectively.¹⁴ The result suggests that the κ -layer has more electrons than the β'' -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 β' - and κ -layer metallic although the κ -layer has considerable charge disproportionation.^{15c} In the anionic layers (Fig. 1d) the anions are all oriented in the same direction and no short contacts were observed between the spin centres of the PO radicals (the shortest O...O distance is 5.880(19) Å). Fig. 1a shows that the sulfonate groups (-SO₃⁻) are oriented to face the β'' -layers and the N-O atoms, which carry the unpaired spin, are oriented to face the κ -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 centre O atom and a sulfur atom of the BEDT-TTF molecule in the κ -layer (O5...S1) of 3.638(10) Å is observed (Fig. 1e),¹⁶ 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. Only the latter is in the range found for the TEMPO radicals (1.27-1.30 Å).¹¹ 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 κ -layer.¹⁷

The electrical resistivity of the single crystals were measured by a conventional four probe method. At 300 K a resistivity of 1.6×10^{-2} Ω-cm was observed. The temperature dependence of the electrical resistivity is shown in Fig. 2. 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 first metal containing an aminoxyl radical, that is stable to such low temperatures.

The electronic structure has been characterised using extended Hückel tight-binding band structure calculations¹⁹ for each of the different 2-dimensional donor sheets. Figure 3 shows Fermi surfaces of the κ - (a and b) and β'' -layers (c and d) at the band filling of 0.80 (a), 0.75 (b), 0.70 (c), and 0.75 (d), respectively. Despite of the difference in the band filling, both Fermi surfaces for the κ and β'' layers are similar to each other. The band dispersion (Figure 1S in the supporting information) of the β'' -layer has no significant mid-gap but that of κ -layer has a mid-gap-like split, suggesting that the κ -layer can become a Mott insulator if the band filling is 0.75.

Figure 2. Temperature-dependent electrical resistivity of **3**.

Figure 3. Calculated Fermi surfaces of κ - (a and b) and β'' -layers (c and d) at the band filling of 0.80 (a), 0.75 (b), 0.70 (c), and 0.75 (d), respectively.

The temperature-dependent magnetic susceptibility of **3** was measured using a Quantum Design SQUID magnetometer from 2-300 K (MPMS-5SH) and from 0.5-2 K (MPMS-XL5 with an IQUANTUM iHelium3 ³He refrigerator). The χ -*T* curve (Figure 4a) has a broad maximum around 1 K, below which χ decreases with decreasing temperature. We also measured the magnetic susceptibility of a bundle of the needle crystals oriented in four glass capillaries (1 mmφ) parallel and perpendicular to the crystal long axis (*//* *b*), but no anisotropy was observed (Figure 2S in the supporting information). The result suggests that the χ drop is not caused by an antiferromagnetic transition. In fact, the powder data (Figure 4a) can be modeled by a 1D Heisenberg *S* = 1/2 alternating chain expression²⁰ 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 BEDT-TTF layers (χ_{ET}) we subtracted the anionic Heisenberg term from the total data. The resultant curve is shown in Figure 4b.²¹ The value of 3.5 – 4.2×10^{-4} emu/mol is in the range expected for Pauli paramagnetic susceptibility of organic metals (2 – 6×10^{-4} emu/mol),¹ suggesting no charge localization on the donor layers and normal metallic behaviour. The small negative *J*

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values indicate that there is a short range weak antiferromagnetic PO...PO interaction. As shown in the inset of Figure 4a, 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 Fig. 1e, suggests that the weak antiferromagnetic interaction is mediated by the κ -type donor layers. Since 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.

Figure 4. Temperature-dependent magnetic susceptibility (χ - T) plot of the powder sample of **3** (a). The dashed line is calculated on the basis of a alternate Heisenberg 1D chain model. Inset shows a 1D chain of the anions. (b) χ - 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.

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 κ - and β'' -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 figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo M.-H. *Organic Superconductor (Including Fullerenes) Synthesis, Structure, Properties and Theory*; Prentice-Hall: New York, 1992.
- (2) Mori, T.; Mori, H.; Tanaka, S. *Bull. Chem. Soc. Jpn.* **1999**, 72, 179.
- (3) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, 117, 12209.
- (4) Coronado, E.; Day, P. *Chem. Rev.* **2004**, 104, 5419. Enoki, T.; Miyazaki, A. *ibid.* **2004**, 104, 5449.
- (5) Kobayashi, H.; Cui, H.; Kobayashi, A. *Chem. Rev.* **2004**, 104, 5265.
- (6) Sugano, T.; Fukasaka, T.; Kinoshita, M.; *Synth. Met.* **1991**, 41-43, 3281. Fujiwara, E.; Aonuma, S.; Fujiwara, H.; Sugimoto, T.; Misaki, Y. *Chem. Lett.* **2008**, 37, 84. Otsubo, S.; Cui, H.; Lee, H.-J.; Fujiwara, H.; Takahashi, K.; Okano, Y.; Kobayashi, H.; *Chem. Lett.* **2006**, 35, 130. Matsushita, M. M.; Kawakami, H.; Sugawara, T.; Ogata, M. *Phys. Rev. B* **2008**, 77, 195208. Sugimoto, T.; Yamaga, S.; Nakai, M.; Ohmori, K.; Tsujii, M.; Nakatsuji, H.; Hosoi, H. *Chem. Lett.* **1993**, 1361. Hutchison, K. A.; Srdanov, G.; Menon, R.; Gabriel, J. -C. P.; Knight B.; Wudl, F. *J. Am. Chem. Soc.* **1996**, 118, 13081. Nakatsuji, S.; Anzai, H.; *J. Mater. Chem.* **1997**, 7, 2161. Nakamura, Y.; Koga, N.; Iwamura, H. *Chem. Lett.* **1991**, 69. Mukai, K.; Senba, N.; Hatanaka, T.; Minakuchi, H.; Ohara, K.; Taniguchi, M.; Misaki, Y.; Hosokoshi, Y.; Inoue, K.; Azuma, N.; *Inorg. Chem.*, **2004**, 43, 566. Aonuma, S.; Casellas, H.; Faulmann, C.; Garreau de Bonneval, B.; Malfant, I.; Cassoux, P.; Lacroix, P.G.; Hosokoshi, Y.; Inoue, K. *J. Mater. Chem.*, **2001**, 11, 337.
- (7) (a) Akutsu, H.; Yamada, J.; Nakatsuji, S. *Chem. Lett.* **2003**, 32, 1118. (b) Akutsu, H.; Yamada, J.; Nakatsuji, S. *Synth. Met.* **2005**, 152, 377. (c) Akutsu, H.; Masaki, K.; Mori, K.; Yamada, J.; Nakatsuji, S. *Polyhedron* **2005**, 24, 2126. (d) Yamashita, A.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Polyhedron* **2005**, 24, 2796. (e) Akutsu, H.; Yamada, J.; Nakatsuji, S.; Turner, S. S. *Solid State Commun.* **2006**, 140, 256. (f) Akutsu, H.; Sato, K.; Yamashita, S.; Yamada, J.; Nakatsuji, S.; Turner, S. S. *J. Mater. Chem.* **2008**, 18, 3313. (g) Akutsu, H.; Yamashita, S.; Yamada, J.; Nakatsuji, S.; Turner, S. S. *Chem. Lett.* **2008**, 37, 882.
- (8) Crystal data for PPh₂·C₃₅H₃₈N₂O₅PS, M = 629.73, Triclinic $P\bar{1}$, a = 11.6417(6), b = 11.7774(7), c = 13.7069(13) Å, α = 112.458(3), β = 99.9654(9), γ = 99.1630(10)°, V = 1657.4(2) Å³, Z = 2, D_c = 1.262 gcm⁻³, $\text{MoK}\alpha$, λ = 0.71073 Å, θ_{max} = 27.5°, T = 295 K, total data 14488, unique data 6879, μ = 0.1893 mm⁻¹, 435 parameters, R = 0.070, R_w = 0.057 on $|F|$ and S = 1.094. The structure was solved by direct methods and all non-H atoms were subjected to anisotropic refinement by full-matrix least-squares on F using CrystalStructure Ver. 3.8.2. (See Supporting Information for further details).
- (9) Shibaeva, R. N. *Zh. Strukt. Khim.*, **1975**, 16, 330.
- (10) Crystal data for **3**: C₃₁H₃₄N₂O₅S₁₇, M = 1059.74, Triclinic $P\bar{1}$, a = 8.711(2), b = 11.8136(4), c = 40.528(7) Å, α = 89.448(2), β = 87.3821(12), γ = 83.2487(9)°, V = 4137.3(12) Å³, Z = 4, D_c = 1.70 gcm⁻³, $\text{MoK}\alpha$, λ = 0.71073 Å, θ_{max} = 27.5°, T = 293 K, total data 27895, unique data 6689, μ = 0.930 mm⁻¹, 989 parameters, R = 0.080, R_w = 0.075 on $|F|$ and S = 1.151. The structure was solved by direct methods and all non-H atoms were subjected to anisotropic refinement by full-matrix least-squares on F using Crystals Ver. 12.86c (See Supporting Information for further details).
- (11) Several BEDT-TTF salts have been reported which have two different donor layers with entirely different structures.¹²
- (12) Schlueter, J. A.; Geiser, U.; Wang, H. H.; Kini, A. M.; Ward, B. H.; Parakka, J. P.; Daugherty, R. G.; Kelly, M. E.; Nixon, P. G.; Winter, R. W.; Gard, G. L.; Montgomery, L. K.; Koo, H. -J.; Whangbo, M. -H. *J. Solid State Chem.* **2002**, 168, 524. Akutsu, H.; Akutsu, A.; Turner, S. S.; Day, P.; Canadell, E.; Firth, S.; Clark, R. J. H.; Yamada, J.; Nakatsuji, S. *Chem. Comm.* **2004**, 18. Akutsu, H.; Yamada, J.; Nakatsuji, S.; Turner, S. S. *Solid State Commun.*, **2007**, 144, 144. Martin, L.; Day, P.; Akutsu, H.; Yamada, J.; Nakatsuji, S.; Clegg, W.; Harrington, R. W.; Horton, P. N.; Hursthouse, M. B.; McMillan, P.; Firth, S. *CrystEngComm* **2007**, 9, 865.
- (13) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, 86, 1973.
- (14) Only a small number of charge-transfer salts have been reported with two crystallographically independent conducting layers each of which have different band fillings.^{15a-c}
- (15) (a) Ishikawa, Y.; Saito, K.; Kikuchi, K.; Kobayashi, K.; Ikemoto, I. *Bull. Chem. Soc. Jpn.* **1991**, 64, 212. (b) Kato, R.; Fujiwara, M.; Kashimura, Y.; Yamaura, J. *Synth. Met.* **2001**, 120, 675. (c) Kawamoto, T.; Mori, T.; Kakiuchi, T.; Sawa, H.; Shirahata, T.; Kibune, M.; Yoshino, H.; Imakubo, T. *Phys. Rev. B* **2007**, 76, 134517.
- (16) The shortest S...O contact between the other crystallographically independent anion **2** and a BEDT-TTF molecule (S15-O10) is 3.989(11) Å.
- (17) An oxidized TEMPO has the shorter N-O distance [e.g. 1.195(5) Å in (TEMPO)(TCNQF₄)].¹⁸
- (18) Nakatsuji, S.; Takai, A.; Nishikawa, K.; Morimoto, Y.; Yasuoka, N.; Suzuki, K.; Enoki, T.; Anzai, H. *Chem. Commun.* **1997**, 275.
- (19) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H.; *Bull. Chem. Soc. Jpn.* **1984**, 57, 627.

(20) Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033.

(21) Note that there is a deviation of the observed data from the best fitting curve in the low temperature region (< 50 K, see Figure 4a). Such uncertainty in the estimation of χ_{ET} at low temperature may indicate that the data does not exactly follow the 1D alternating chain model.

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κ - β'' -(BEDT-TTF)₂(PO-CONHC₂H₄SO₃) is the first stable metal containing an aminoxyl radical. The salt has both κ - and β'' -type donor sheets and exhibits metallic behavior down to 1.7 K. The magnetic susceptibility can be modeled by an alternate chain model with $J_1 = -0.80$, and $J_2 = -0.69$ K.