The first organic paramagnetic metal containing the aminoxyl radical[†]

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We have prepared an organic magnetic anion, PROXYL-4-CON-HCH₂SO₃⁻ (1). The electrocrystallisation of BEDT-TTF with PPh₄1 gave the first purely organic paramagnetic metal, β'' -(BEDT-TTF)₂(1). The salt shows a broad metal-insulator transition at approximately 210 K.

Since the first synthesis of the donor molecule BEDT-TTF (bis (ethylenedithio)tetrathiafulvalene, ET) three decades ago,¹ many ET-based conducting salts with a wide variety of anions have been prepared.² In the salts, the donor molecules usually form quasi-2-D conducting layers, which are separated by the counteranions.³ Usually the anions play no significant role in the transport properties and prevent the donors from approaching one another in the crystals. In fact, a salt with smaller anions is usually a more stable metal than an isomorphous salt with larger anions.

Since the discovery of the paramagnetic organic superconductor, β'' -(ET)₄[(H₃O)Fe(C₂O₄)₃]·PhCN,⁴ organic magnetic conductors have attracted great interest.^{5,6} In particular, λ -(BETS)₂FeCl₄ and its derivatives show unique physical properties.⁵ Their interesting properties emerge from interactions between magnetic moments incorporated into a conducting crystal. However, magnetic interactions in these salts are small, probably because the magnetic centres (here transition metals) are surrounded by ligands such as Cl⁻, Br⁻, C₂O₄²⁻, *etc.*, through which the centres must interact indirectly.

Alternatively organic free radicals can be used as the source of unpaired electron density. The spin is delocalised over a few atoms on a 'bare' orbital. Therefore, the orbital containing the unpaired electron can potentially overlap directly with orbitals occupied by conduction electrons. For this reason many researchers have introduced organic radicals into organic conducting salts but all reported salts have only shown semiconducting behaviour until now.⁷

Our recent focus is on preparing new organic magnetic anions that combine the organic free radical TEMPO with the sulfonate group $(-SO_3^{-})$.⁸ However, all of the ET-based salts of these anions show only semiconducting behaviour. As mentioned above, smaller anions usually provide more conductive and/or metallic salts. Therefore, we have chosen the smaller PROXYL radical. We have now prepared an organic magnetic anion, PROXYL-CONHCH₂SO₃⁻ (1) which is the smallest sulfonate that we have thus far prepared. We have been able to synthesise the ET salt of 1, the structure and properties of which are reported in this communication.



The acid **1** was prepared by reacting 3-carboxy-PROXYL (0.40 g, 2.1 mmol) with H₂NCH₂SO₃H (0.29 g, 2.6 mmol) in the presence of N,N'-dicyclohexylcarbodiimide (DCC, 0.53 g, 2.6 mmol) and 4-dimethylaminopyridine (DMAP, 0.63 g, 5.2 mmol) in 30 mL of dichloromethane at ambient temperature with stirring over four days. Metathesis of H**1** with PPh₄Br yielded PPh₄**1** (**2**) as yellow crystals, which were then recrystallised from acetonitrile (yield 27%). X-Ray diffraction data of **2** were collected on a Rigaku AFC-5R 4-circle diffractometer at room temperature.[‡] The asymmetric unit contains one PPh₄ cation and one anion. The N–O distance in the PROXYL part is 1.272(3) Å, which is similar to the corresponding distance in TEMPO radicals (1.27–1.30 Å).⁹ The temperature-dependent magnetic susceptibility of a polycrystalline sample from 2–300 K using a Quantum Design MPMS-5S SQUID magnetometer obeys the Curie–Weiss law with C = 0.379 emu K mol⁻¹ and $\theta = -0.36$ K.

The conventional constant-current electrocrystallisation in a mixed solvent of *m*-dichlorobenzene and acetonitrile with 15 mg of ET and 70 mg of **2** gave black block-like crystals. The X-ray diffraction measurement was performed on a Rigaku AFC-5R 4-circle diffractometer at ambient temperature. The resulting data were solved as β'' -(ET)₂**1** (**3**).§ A donor to anion ratio of 2 : 1 indicates that each ET molecules has a formula charge of +1/2. The crystal structure of **3** shown in Fig. 1 has an asymmetric unit with two ET molecules and



Fig. 1 An ORTEP view (50% probability level) of β'' -(ET)₂1 (3) along the *c*-axis.

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Fig. 2 Packing arrangement of the donor layer in 3 (ORTEP, 50% probability ellipsoids). Dashed lines indicates S···S contacts shorter than the van der Waals distance (<3.7 Å).

one anion. The N-O distance of the PROXYL moiety in 3 is 1.274(10) Å, which is the same as that in 2. The unit cell consists of alternating donor/anion layers along the b-axis. In the anion layer, there is a PROXYL spin dimer about the centre of symmetry with a short O···O contact of 4.649(10) Å. In addition, the observed shortest contact between the oxygen atom of the PROXYL moiety and sulfur atoms of ET molecules is 3.570(8) Å, which is 0.2 Å longer than sum of the van der Waals radii (3.37 Å). The structure suggests that it is unlikely that the salt shows significant interactions between conducting and magnetic electrons. The donor layers are in a β'' -type packing motif as shown in Fig. 2. The central C=C distances of the two crystallographically independent donor molecules (A and B shown in Fig. 2) are almost the same, 1.367(10) and 1.368(10) Å, respectively. The estimated charges on both ET molecules calculated using bond lengths¹⁰ are also almost the same, +0.50 and +0.49, respectively. In other words the positive charge is equally distributed over the donor layer and not localised as in charge disproportionation. The electronic structure has been characterised using extended Hückel tight-binding band structure calculations on the 2-dimensional ET sheet.¹¹ The calculated values of the intermolecular overlap integrals $(\times 10^{-3})$ p1, p2, p3, a1, a2, s1, s2 and s3 (see Fig. 2) are -6.34, -4.73, -1.62, -8.21, -9.18, -10.23, -16.45 and -10.25, respectively. The values of a1, a2, s1, s2 and s3 are larger than those of p1, p_2 and p_3 , indicating that the side-by-side interactions are stronger than the face-to-face interactions. The dispersion relation (Fig. 3, left)



Fig. 3 Electronic band structure calculated for 3.

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Fig. 4 Temperature dependence of electrical resistivity for **3**. Inset is the expansion from 160–290 K.

and Fermi surfaces (Fig. 3, right) are shown. Only small hole and electron pockets are observed, which is common for β'' -type salts.¹² β'' -Type ET salts are usually semimetals or 'weak' metals.

The temperature-dependent electrical resistivity of 3 measured by the four-probe AC method is shown in Fig. 4. The resistivity gradually falls with decreasing temperature, indicating metallic conductivity (see inset in Fig. 4). Thus, this is the first aminoxyl-radical containing organic conductor that shows metallic transport. The resistivity reaches a minimum at approximately 210 K, increasing gradually down to 150 K, and then increasing rapidly as for a semiconductor. Fig. 5a shows the $\chi T-T$ plot of 3. If the PROXYL radicals had non-interacting spin moments and the ET molecules were magnetically silent, the $\chi T-T$ plot would be a horizontal line, with $\chi T = 0.352$ emu K mol⁻¹ (=94% of s = 1/2 spin (0.375 emu K mol⁻¹)) as shown in Fig. 5a. However, the actual magnetic curve deviates from the straight line in two regions, (i) low temperature region (<20 K) and (ii) high temperature region (>120 K), as shown in Fig. 5a. The data in the range of 2-20 K (i) can be modelled by the Curie–Weiss law with C = 0.352 emu K mol⁻¹ and $\theta = -1.05$ K. The C value is 94% of that of the s = 1/2 spin (0.375 emu K mol⁻¹) on



Fig. 5 (a) $\chi T-T$ plot for salt 3 where χ is the magnetic susceptibility per half of the unit cell [(ET)₂1]. The solid horizontal line is drawn at $\chi T = 0.352$. (b) χ -T plot after subtracting the Curie term [$\chi_{\text{Curie-Weiss}} = 0.352/(T - 1.05)$] from the total susceptibility.



Fig. 6 Temperature dependent electrical resistivities of 3 under pressure. Inset shows pressure dependence of the slopes of the Arrhenius plots (250-300 K) which are equal to the activation energy for semiconductors.

the PROXYL moiety, suggesting that this part of the salt dominates the Curie-Weiss term. It is also likely that the Weiss constant of -1.05 K is caused by some small antiferromagnetic interaction between the PROXYL moieties. Actually, the structure shows that the anions form spin dimers with a short >N-O···O-N< contact. The deviation in the high temperature region (ii) may be a contribution from the ET cations. To obtain the temperature dependence of the contribution, we subtracted the Curie-Weiss term from the total data. The resultant magnetic susceptibility curve is shown in Fig. 5b. The magnetic susceptibility at 300 K is 3×10^{-4} emu mol⁻¹ which compares well to the Pauli paramagnetic susceptibility of usual organic metallic conductors $(2-6 \times 10^{-4} \text{ emu mol}^{-1})$.³ This is consistent with the metallic transport property of the salt at room temperature. The magnetic susceptibility gradually decreases with decreasing temperature to $0-1 \times 10^{-4}$ emu mol⁻¹. Since the absolute susceptibility is proportional to the density of states (DOS), the gradual decrease corresponds to a decrease in DOS, which is consistent with the broad MI transition. The upturn below 120 K suggests the transition is not caused by a density wave but is due to charge ordering, which is also common to β'' -type salts.^{12,13} We have therefore not found any evidence of an interaction between the localised spins and the conduction electrons.

The electrical resistivity under pressure up to 15 kbar was measured using a clamp-type pressure cell (Fig. 6), in order to expand the metallic region. However, the resistivity under static pressure has no metallic regions and the activation energies increase with increasing pressure as shown in the inset of Fig. 6. Uniaxial stress may expand the metallic region.

In conclusion, the smallest purely organic paramagnetic anion provides the first organic paramagnetic metal containing the aminoxyl radical. The salt shows metallic behaviour down to 210 K, followed by a broad metal–insulator transition.

Notes and references

[‡] Crystal data for **2**: C₃₄H₃₈N₂O₅P₁S₁, M = 617.72, triclinic $P\overline{1}$, a = 12.042(3), b = 12.306(3), c = 11.691(4) Å, $\alpha = 95.75(3)$, $\beta = 111.52(2)$, $\gamma = 83.20(2)^\circ$, V = 1597.4(8) Å³, Z = 2, $D_c = 1.284$ g cm⁻³, MoKα, $\lambda = 0.71073$ Å, $\theta_{max} = 27.5^\circ$, T = 294 K, total data 7690, unique data 7342, $\mu = 0.195$ mm⁻¹, 426 parameters, R = 0.052, $R_w = 0.061$ on |F| and S = 1.025. 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. CCDC 685677.†

§ Crystal data for **3**: C₃₀H₃₄N₂O₅S₁₇, M = 1047.63, triclinic $P\overline{1}$, a = 12.436(4), b = 19.528(6), c = 9.326(3)Å, $\alpha = 97.06(3), \beta = 110.22(3),$ $\gamma = 83.44(3)^\circ, V = 2102.9(12)$ Å³, $Z = 2, D_c = 1.654$ g cm⁻³, MoKα, $\lambda = 0.71073$ Å, $\theta_{max} = 27.5^\circ, T = 295$ K, total data 10383, unique data 9644, $\mu = 0.9138$ mm⁻¹, 521 parameters, R = 0.064 $R_w = 0.068$ on |F| and S = 1.134. 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. CCDC 685678.†

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