A New Organic Anion Consisting of the TEMPO Radical for Organic Charge-Transfer Salts: 2,2,6,6-Tetramethylpiperidinyloxy-4-sulfamate (TEMPO-$NHSO_3^-$)

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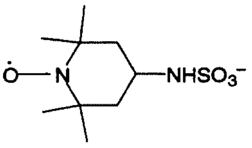
The title organic anion was prepared as its tetraphenylphosphonium salt, (Ph_4P)(TEMPO-$NHSO_3$), which reacted with $(TTF)_3(BF_4)_2$ to give (TTF)(TEMPO-$NHSO_3$), which shows the Curie–Weiss behavior (C = 0.360 emu K mol^{-1} and θ = –0.52 K) with weak antiferromagnetic interaction. This magnetic behavior is found to be attributed to the TEMPO radical.

Over the past decade, the interesting potential of molecular-based organic conductors has been considered to lie on the possibility to create charge-transfer (CT) materials in which conductivity coexists with the local magnetic moments. The recently reported strategies for introducing a magnetic part into CT materials involve the use of (i) magnetic anions as a counter component of CT salts,[1,2] (ii) π-electron donors carrying stable organic radicals,[3,4] and (iii) organic counter cations derived from the TEMPO radical.[5,6] An alternative candidate in this regard is to employ organic counter anions with local magnetic moments, but the materialization of CT salts containing such anions has not yet been reported. Thus, we attempted to prepare a new organic anion consisting of the TEMPO radical, TEMPO-$NHSO_3^-$, as its tetraphenylphosphonium salt (Ph_4P)(TEMPO-$NHSO_3$) (**1**). In this paper, we report the preparation, crystal structure and magnetic properties of **1**. We also disclose the crystal structure and physical properties of the tetrathiafulvalene (TTF) salt with TEMPO-$NHSO_3^-$, (TTF)(TEMPO-$NHSO_3$) (**2**), which is the first organic CT salt containing a stable organic radical in an anion part.



TEMPO-$NHSO_3^-$

4-Amino-TEMPO was successively treated with chlorosulfonic acid in dichloromethane at 0–5 °C and aqueous NaOH to yield TEMPO-$NHSO_3Na$. Exchange of the counter cation with tetraphenylphosphonium chloride for increasing the solubility in organic solvent gave **1** as orange block-like crystals after recrystallization from CH_2Cl_2–toluene (overall yield 32%). Elemental analysis of **1** indicates that the crystals were hydrated with the composition (Ph_4P)(TEMPO-$NHSO_3$)$(H_2O)_{1.7}$.[7]

The crystal structure of the hydrated **1** by X-ray analysis is shown in Figure 1.[8] It contains one Ph_4P^+ cation, one TEMPO-$NHSO_3^-$ anion, one lattice water molecule (W1), and an additional lattice water molecule (W2) with the occupancy of 0.63 per asymmetric unit. Accordingly, the total amount of the water molecules is 1.63, which is comparable to that calculated from the elemental analysis. The sulfamate groups of two inversion-related TEMPO-$NHSO_3^-$ anions overlap each other with two N–H···O–S hydrogen bonds to form a dimer, in which the two aminoxyl radical groups are far out of that cyclic hydrogen-bonded bis-sulfamate part in opposite directions. The lattice water molecules (W1 and W2) are located between dimers, forming O–H···O hydrogen bonds with the oxygen atoms of sulfamate and aminoxyl groups to link the dimers in a three-dimensional (3D) fashion. The Ph_4P^+ cation exists within a hollow space of the 3D network. Therefore, it is impossible to discern the close contact of the aminoxyl radical groups of the TEMPO-$NHSO_3^-$ anions, which causes a significant magnetic exchange interaction, within a dimer and between dimers. In fact, temperature dependence of magnetization for this compound measured by SQUID magnetometer is almost reproduced by the Curie–Weiss law with a Curie constant of C = 0.384 emu K mol^{-1} and a Weiss temperature of θ = –0.034 K.

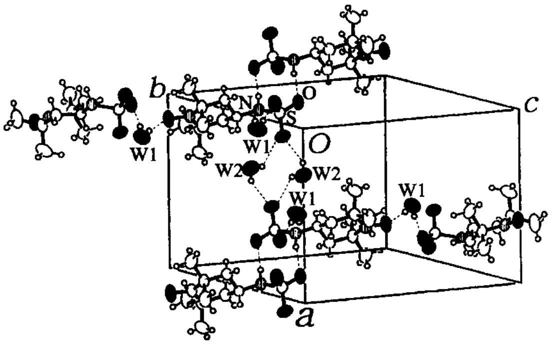


Figure 1. The crystal structure of the hydrated **1**. Dark and striped circles show the O and N atoms, respectively, and dashed lines indicate hydrogen bonds. The Ph_4P^+ cations are omitted for clarity.

Mixing acetone solutions of **1** (0.32 mmol) and $(TTF)_3(BF_4)_2$ (0.17 mmol) at room temperature gave the black powder of **2** (95% yield based on **1**),[9] and a transparent plate-like single crystal of **2** appropriate for X-ray study was obtained from an acetonitrile solution of **1** and $(TTF)_3(BF_4)_2$ which was allowed to stand in a refrigerator. This salt has a monoclinic structure incorporating one TTF molecule and one TEMPO-$NHSO_3^-$ anion per asymmetric unit.[10] As shown in Figure 2(a), the TTF molecules form centrosymmetric face to face dimers (interplanar distance, 3.34 Å), which are separated by the sulfamate groups of two TEMPO-$NHSO_3^-$ anions along the *a* axis. There are intermolecular S···O contacts shorter than the van der Waals distance (3.32 Å; Bondi) between the TTF dimer and the adjacent sulfamate groups. The TTF dimers do not form a column (see Figure 2(b)), and are surrounded by the TEMPO-$NHSO_3^-$ anions in the *bc* plane. No contact interaction between the TTF dimers can therefore be observed, which is certainly

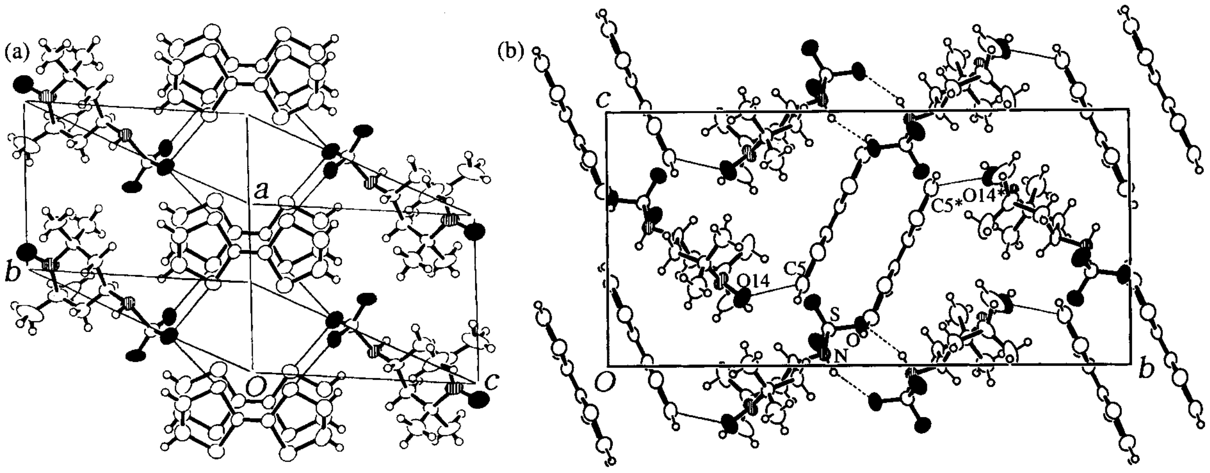


Figure 2. The packing diagram of (TTF)(TEMPO-NHSO$_3$) (a) and the projection along the *a* axis (b), where dark and striped circles show the O and N atoms, respectively; (a) solid lines indicate short S···O contacts, (b) dashed and solid lines indicate hydrogen bonds and short C···O contacts, respectively, and atoms with label suffix * are related by an inversion center to those without the suffix.

responsible for the diamagnetic property of the TTF dimer as well as a high room-temperature resistivity (> 10^6 Ω·cm) of **2**. The sulfamate groups of two TEMPO-NHSO$_3^-$ anions in this salts are also interlinked via N–H···O-S hydrogen bonds to form a cyclic hydrogen-bonded structure similar to that found in the crystal structure of **1**. In addition, the N–O distance of the TEMPO radical part is 1.274(7) Å, which corresponds well to that of the reported neutral TEMPO radicals (1.27–1.30 Å).[11] In general, when the aminoxyl radical of TEMPO is oxidized, the N–O distance becomes shorter than that of the neutral one due to the $>N^+=O$ double bond formation, as can be found in the case of (TEMPO)(TCNQF$_4$) [the N–O distance, 1.195(5) Å].[5] Therefore, it appears that the TEMPO radical part is not oxidized, which is also supported by the fact that the >N–O part has a pyramidal form.

The magnetic susceptibility of powder sample of **2** obeyed the Curie–Weiss law with $C = 0.360$ emu K mol^{-1} and $\theta = -0.52$ K. The value of the Curie constant suggests the presence of one spin in the asymmetric unit. The powder sample of **2** exhibited a single ESR line at $g = 2.0076$ with a peak to peak line width of 11.5 Oe at room temperature. This *g* value is very close to that of (Ph$_4$P)(TEMPO-NHSO$_3$) ($g = 2.0068$) and regarded as a reasonable value for the general aminoxyl radicals ($g = 2.006$),[5] suggesting that the observed ESR signal can be expected to arise mainly from the TEMPO group but not the TTF cation-radical (TTF$^{\bullet+}$), because the spins on the TTF sites are compensated each other by the above-mentioned diamagnetic dimerization. The origin of the weak antiferromagnetic interaction with a Weiss constant of $\theta = -0.52$ K in this salt may be attributed to the contacts O14···C5 and O14*···C5* [3.00(1) Å < van der Waals distance (3.22 Å)] observed between the TTF dimer and the two neighboring aminoxyl groups [N–O···TTF···TTF···O–N, see Figure 2(b)]. According to the intermolecular spin-polarization,[12] these contacts permit an antiferromagnetic interaction, ON(↑)···TTF(↓)···TTF(↑)···ON(↓), so that the TTF dimers appear to play an important role in the weak antiferromagnetic coupling pathway. The preparation of CT salts with other organic donors and ionic crystals with magnetic and/or non-magnetic cations is in progress.

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References and Notes

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7 Anal. Found: C, 63.84; H, 6.64; N, 4.50%. Calcd for $C_{33}H_{41.4}N_2O_{5.7}PS$: C, 63.89; H, 6.73; N, 4.52%.

8 Crystal data for the hydrated **1** at room temperature: monoclinic, space group $P2_1/c$ (No. 14), formula $C_{33}H_{41.26}N_2O_{5.63}PS$, fw 619.07, $a = 10.724(3)$, $b = 21.598(2)$, $c = 14.150(2)$ Å, $\beta = 91.78(2)°$, $V = 3275.9(9)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.255$ Mg m^{-3}, $R = 0.053$, $R_w = 0.053$ for 4560 reflections with $I_0 > 3\sigma(I)$, 516 parameters, $GOF = 2.38$.

9 Anal. Found: C, 39.54; H, 4.87; N, 6.10%. Calcd for $C_{15}H_{22}N_2O_4S_5$: C, 39.62; H, 4.88; N, 6.16%.

10 Crystal data for **2** at room temperature: monoclinic, space group $P2_1/c$ (No. 14), formula $C_{15}H_{22}N_2O_4S_5$, fw 454.65, $a = 7.733(2)$, $b = 23.574(5)$, $c = 11.256(3)$ Å, $\beta = 99.54(2)°$, $V = 2023.4(8)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.492$ Mg m^{-3}, $R = 0.069$, $R_w = 0.065$ for 1761 reflections with $I_0 > 2\sigma(I)$, 301 parameters, $GOF = 1.42$.

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