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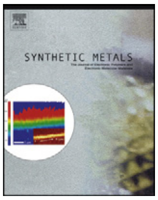

A new BEDT-TTF-based organic metal with an anionic weak acceptor 2-sulfo-1,4-benzoquinone

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ABSTRACT

An anionic weak acceptor, 2-sulfo-1,4-benzoquinone, has provided a new BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) salt $(BEDT\text{-}TTF)_2(2\text{-sulfo-1,4-benzoquinone})\cdot H_2O$. Single crystal X-ray analysis indicates that the unit cell has two crystallographically independent donor layers, one of which has a β″-type packing motif and the other being disordered. Population analysis and SQUID magnetometry suggests that non-β″-layer has an α‴-type packing motif. The dual-layered salt shows metallic behavior with a metal–insulator transition at 90 K.

1. Introduction

Over the past two decades, several organic conductors having two crystallographically independent donor layers have been developed [1–14]. Recently, Schlueter et al. reported a new organic superconductor, κ-α′-$(BEDT\text{-}TTF)_2Ag(CF_3)_4$(1,1,2-trichloroethane) [12]. The salt has dual donor layers of κ- and α′-type arrangements. The authors stated that the salt has a T_C five times higher than that of its polymorph that contains only κ-type arrangements. We also recently reported two dual-layered salts, κ-β″-$(BEDT\text{-}TTF)_2(PO\text{-}CONHC_2H_4SO_3)$ [13] and $(TTF)_3(PO\text{-}CON(CH_3)C_2H_4SO_3)_2$ [14] where PO = 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl free radical. In both salts, the anisotropic anions form head-to-head arrangements in the anionic layers, which not only give dual donor layers but also lead to dipole electric fields, which provide different oxidation states (band filling) for each donor layers. This suggests that the polarity of the anion layer provides hole and electron doping effects for the donor layers.

In 1951 Mulliken classified charge-transfer (CT) complexes into two categories, 'weak' and 'strong' complexes [15]. The 'weak' complexes usually contain alternating donor and acceptor molecules and therefore tend to be poor conductors. The 'strong' complexes usually have 1D or 2D conducting donor and/or acceptor layers, whose electric transport ranges from insulating through semiconducting to metallic and even superconducting [16]. During the past five years, we have focused on preparing new CT complexes with coexisting 'weak' and 'strong' CT interactions. The rationale is that a 'strong' CT salt having a 'weak' CT interaction may yield a partial hole or electron doping effect [11,17,18], which should lead to a drastic increase in electrical conductivity, as observed in metal oxide chemistry [19]. With this in mind, we have previously prepared anionic weak acceptors (caam, bcam, baam, and cas in Scheme 1), all of which provided BEDT-TTF salts [11,17,18]. However, we have not yet found any distinct doping effects in these salts. Furthermore, all salts are semiconductors or weak metals probably because the sizes of the prepared anions are relatively large [13,20,21]. In this letter, we introduce the anionic acceptor, 2-sulfo-1,4-benzoquinone (qs), which is the smallest of all the anionic acceptors we have prepared. It gives a BEDT-TTF salt, the crystal structure and physical properties of which are reported.

2. Experimental

The potassium salt of qs was prepared according to the literature method [22]. Metathesis of Kqs with PPh_4Br gave PPh_4qs (**1**) as orange crystals, which were then recrystallized from acetone (yield 25%). Cyclic voltammogram was registered on an ALS 612C electrochemical analyzer. Elongated plate-like single crystals of the BEDT-TTF salt (**2**) were obtained by the controlled-current electrocrystallization method [23,24] in 15 mL of PhCl with 15 mg of BEDT-TTF and 70 mg of **1**. Poorer quality crystals were also obtained by the conventional constant-current method using H-cell in PhCl. Single crystal X-ray diffraction data of **1** [25] and **2** [26] were collected with a Rigaku AFC-7R diffractometer equipped

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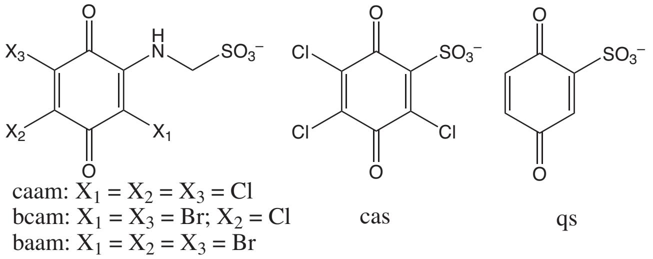

Scheme 1.

with an ADSC Quantum1 CCD area detector, at room temperature. X-ray diffraction data of **2** at 70 and 110 K were collected with a Rigaku 4176F07 diffractometer. The electrical resistivity of single crystals was measured by a conventional four probe method using a HUSO HECS-994C multi-channel conductometer. The magnetic susceptibility of a polycrystalline sample from 2 to 300 K was measured using a Quantum Design MPMS-5SH SQUID magnetometer. The data were corrected for the contribution of the sample holder (aluminum foil) and diamagnetic contributions were estimated from Pascal's constants. The ESR spectrum of a single crystal was obtained on a JEOL JES-FE3XG spectrometer, at room temperature. The *g*-value was determined using a Mn^{2+}/MgO marker as an internal standard.

3. Results and discussion

3.1. PPh_4 salt

The crystal structure of **1** is shown in Fig. 1. In the crystal of PPh_4qs (**1**), one PPh_4 cation and one anion are crystallographically independent. For the anion one of the C=O bond lengths is shorter than the other: 1.219(6) Å compared to 1.231(6) Å. This suggests that the introduction of the sulfonate forces the quinone skeleton to become asymmetric. A similar asymmetry was observed for the C=C bonds in the anion's six-membered ring, which are 1.324(5) and 1.298(7) Å. The redox properties of the qs anion together with benzoquinone (BQ) and chloranil (CA) were determined by cyclic voltammetry, and the results are given in Table 1. The E_1 value of qs is slightly lower than that of BQ and 0.54 V lower than that of CA. This suggests that the smallest anion, qs, is the weakest electron acceptor of all the anionic acceptors we have ever prepared [11,17,18]. The electron accepting strength appears to be too weak to accept any fraction of an electron from donors when the qs anion is incorporated in CT salts.

Table 1
Reduction potentials of PPh_4qs.

Compound	E_1	E_2	$\Delta E = \lvert E_2 - E_1 \rvert$
PPh_4qs	−0.55	−1.01	0.46
BQ	−0.52	−0.97	0.45
CA	+0.01	−0.73	0.74

V vs saturated calomel electrode (SCE) in CH_3CN with 0.1 M Bu_4NClO_4, glassy carbon electrode, at room temperature, under N_2, scan rate 50 mV s^{-1}, BQ = benzoquinone, CA = chloranil.

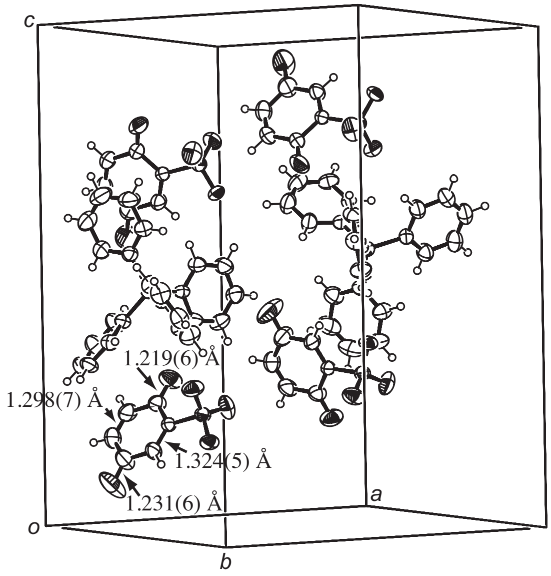

Fig. 1. Crystal structure of **1**.

3.2. BEDT-TTF salt

The structure of the BEDT-TTF salt (**2**) was solved as (BEDT-TTF)$_2$qs·H_2O. However, successive refinement did not give an *R*-value of less than 20%. On applying the merohedral twin law during refinement, an *R*-value of 17.1% was achieved. Due to the relatively high *R*-value, we limit our discussion to the gross molecular arrangement. The crystal structure of **2** is shown in Fig. 2. The asymmetric unit has two BEDT-TTF molecules (A and B), one anion qs and one water molecule. A donor:anion ratio of 2:1 indicates that each BEDT-TTF molecule has a formula charge of +0.5. There are two independent donor layers, each of which consists of either molecules that we have labeled A or B. In the A-layer, for each BEDT-TTF, the eight S atoms are disordered with each atom refined over two positions. This seems to be a discrete positional disorder of two molecular arrangements (A1 and A2) as schematically shown in Fig. 3. The refined site occupancies indicate that the ratio of A1 to A2 is 0.628:0.372 or approximately 2:1. It is not likely to be geometrically possible that the A1 and A2 molecules coexist in the same stack column. Thus a stack column has only an A1 or A2 molecule. Because the ratio of A1 to A2 is approximately 2:1, the ratio of the A1 and A2 containing columns is also 2:1. Over the more than 30-year history of BEDT-TTF chemistry, the donor packing motifs have been classified into several types designated by the labels, α-, β-, α′-, β′-, β″-, α‴-, θ-, κ-, etc. [16,27] and of these only an α‴-type packing motif (Fig. 4) has the corresponding structural features. As shown in Fig. 3, the α‴-type packing motif has a 2:1 ratio of different BEDT-TTF columns. If the three stacks are combined and averaged into one stack, the resultant structure would be similar to the disordered structure in **2**. In this case the size of the unit cell in the side-by-side direction (//*a*) would be increased by three times. We carefully checked all X-ray photographs measured at room temperature but we were not able to find any extra spots or diffuse streaks that indicate the three-folded structure. Then we collected the X-ray diffraction data at 70 and 110 K. X-ray photographs at both temperatures have extra spots indicating the three-folded

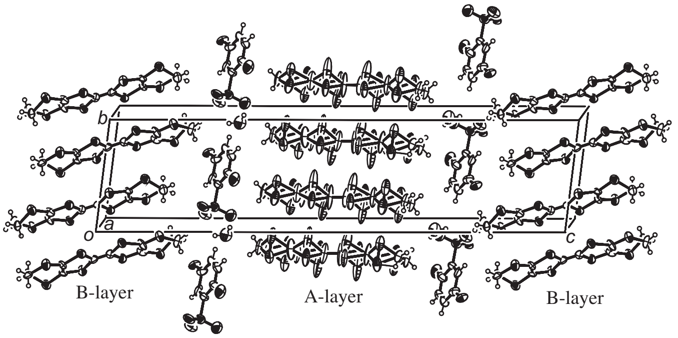

Fig. 2. Crystal structure of **2**.