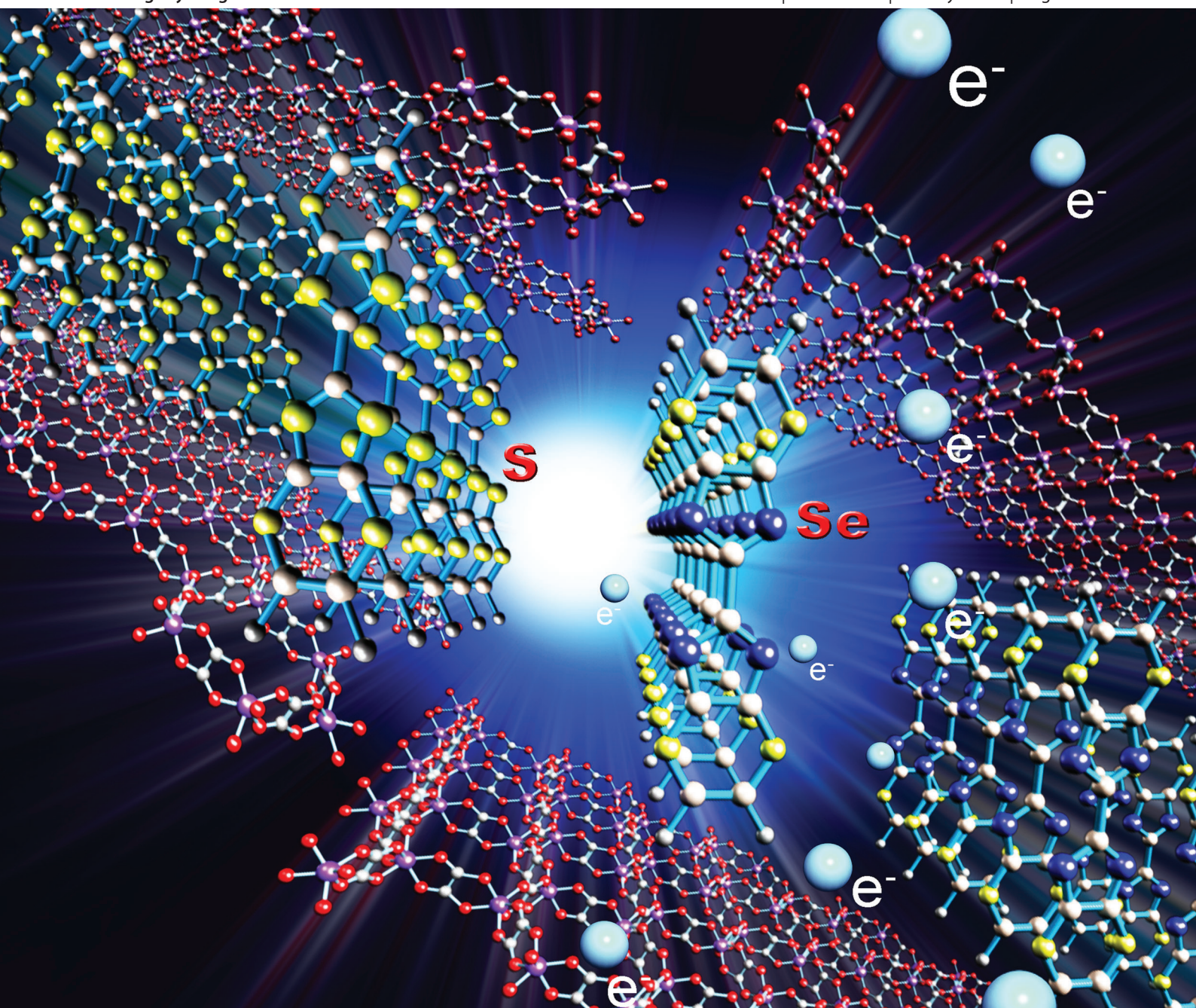


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**COVER ARTICLE**

Zhang *et al.*

$\text{BETS}_3[\text{Cu}_2(\text{C}_2\text{O}_4)_3](\text{CH}_3\text{OH})_2$ : an organic–inorganic hybrid antiferromagnetic metal (BETS = bisethylenetetraselenfulvalene)

## PAPER

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# BETS<sub>3</sub>[Cu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>3</sub>OH)<sub>2</sub>: an organic–inorganic hybrid antiferromagnetic metal (BETS = bisethylene(tetraselenfulvalene))†

Cite this: *CrystEngComm*, 2013, 15, 3529Bin Zhang,<sup>\*a</sup> Yan Zhang,<sup>b</sup> Zheming Wang,<sup>c</sup> Song Gao,<sup>c</sup> Yanjun Guo,<sup>d</sup> Fen Liu<sup>e</sup> and Daoben Zhu<sup>a</sup>

The organic–inorganic hybrid charge-transfer salt of BETS and a two-dimensional oxalate–metalate: BETS<sub>3</sub>[Cu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>3</sub>OH)<sub>2</sub> (**1**) was obtained by the electrochemical oxidation of neutral BETS in the presence of [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> in a C<sub>6</sub>H<sub>5</sub>Cl–CH<sub>3</sub>OH solution. **1** crystallizes in a triclinic crystal system with cell parameters:  $a = 8.7716(3) \text{ \AA}$ ,  $b = 16.9903(6) \text{ \AA}$ ,  $c = 20.5716(7) \text{ \AA}$ ,  $\alpha = 104.794(2)^\circ$ ,  $\beta = 102.209(2)^\circ$ ,  $\gamma = 92.243(2)^\circ$ ,  $V = 2883.1(2) \text{ \AA}^3$  and  $P1$  in 293 K. Donor layers and Jahn–Teller distorted honeycomb anions stack alternatively along the  $c$  axis in **1**. The crystal structure of **1** is similar to the reported compound [BEDT–TTF]<sub>3</sub>[Cu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>3</sub>OH)<sub>2</sub> (BEDT–TTF = bis(ethylene-dithio)tetrathiafulvalene, ET). Compared with the BEDT–TTF salt, the  $c$  axis expands by 2.3% at room temperature, the shorter interaction between the donor molecules increases, the room temperature conductivity increases from  $4 \text{ S cm}^{-1}$  to  $140 \text{ S cm}^{-1}$  and the antiferromagnetic interaction between the metal atoms with Jahn–Teller distortion through the oxalato-bridge enhances.

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## Introduction

Organic–inorganic hybrids provide the possibility of constructing new material with interesting properties, such as metals and superconductors.<sup>1</sup> The organic–inorganic hybrid molecule-based materials, combining a conducting building block ( $\pi$ -unit) from an organic conductor and an inorganic magnetic building block from a molecule-based magnet, play a key role in developing materials that approach conventional room temperature alloys or inorganic magnetic conductors. Because of their application in molecular electronics and spintronics, the rational design of dual-functional organic–inorganic hybrid molecular-based materials is currently challenging to chemists.<sup>2</sup> The oxalate (C<sub>2</sub>O<sub>4</sub><sup>2−</sup>) anion, one of the most commonly used short connectors, plays an important role in molecule-based magnetism, molecular conductors and organic–inorganic hybrid molecule-based magnetic conductors.<sup>3–6</sup> The first organic superconductor containing a mag-

netic anion, [BEDT–TTF]<sub>4</sub>[(H<sub>3</sub>O)Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](C<sub>6</sub>H<sub>5</sub>CN), was discovered in 1995. The coexistence of ferromagnetism and metallic conductivity was observed in organic–inorganic molecular crystals of (BEDT–TTF)<sub>3</sub>[CrMn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sub>x</sub> and BETS<sub>3</sub>[CrMn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sub>x</sub> (BETS = bis(ethylenedithio)-tetra-selenafulvalene) in 2000 and 2003.<sup>7</sup> More recently, the semiconductor (BEDT–TTF)<sub>3</sub>[Cu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>3</sub>OH)<sub>2</sub> was discovered and an antiferromagnetic interaction between the Jahn–Teller distorted oxalate-bridged Cu<sup>2+</sup> atoms was observed.<sup>8</sup>

BETS is a stable organic molecule like BEDT–TTF, with the S atom in the inner five-membered rings replaced by Se and it is one of the most important building blocks of organic conductors (Scheme 1).<sup>9</sup> The greater atomic radius of Se and its more diffuse electron cloud enhance the molecular overlap between the donor molecules, thereby enhancing the conductivity for a given structure. Thus, interesting conducting and magnetic properties of the organic–inorganic hybrid charge-transfer salt of BETS and [Cu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>n</sub> are expected.

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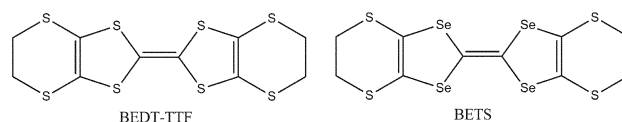
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Scheme 1 BEDT–TTF and BETS molecules.



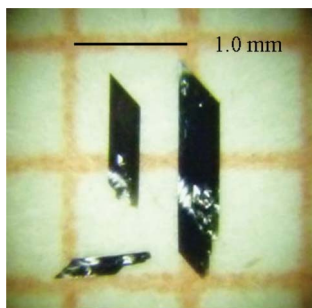


Fig. 1 The morphology of crystal 1.

## Experiments

BETS was synthesized by a reported method.<sup>10</sup>  $\text{C}_6\text{H}_5\text{Cl}$  was dried over  $\text{CaCl}_2$  and freshly distilled prior to use.  $\text{CH}_3\text{OH}$  was freshly distilled before use.

$(\text{Et}_3\text{NH})_2\text{Cu}(\text{C}_2\text{O}_4)_2$  was obtained from a methanol solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Et}_3\text{N}$ .

5.0 mg of BETS and 30.0 mg of  $(\text{Et}_3\text{NH})_2\text{Cu}(\text{C}_2\text{O}_4)_2$  were dissolved in a mixture of 25.0 ml of distilled  $\text{C}_6\text{H}_5\text{Cl}$  and 5.0 ml of distilled  $\text{CH}_3\text{OH}$  and placed in an electrocrystallization cell. The cell was subjected to a constant source of 0.70  $\mu\text{A}$  for 2 weeks at room temperature. Shiny black, thin plate crystals were obtained on the cathode with a yield of 80% (Fig. 1).

A piece of a single crystal was selected for X-ray diffraction. Data was collected at 293 K on a Nonius Kappa CCD with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation.<sup>11</sup> The crystal structure was solved by the direct method, the hydrogen atoms of the ethylene groups were found by calculation and the hydrogen atoms of the solvent molecules were omitted. Atoms of the solvent molecules were disordered. All of the nonhydrogen atoms were refined anisotropically.<sup>12</sup>

Magnetization measurements were performed on a polycrystalline sample tightly packed in a Al bag on a Quantum Design MPMS 7XL System. Magnetic susceptibility data was corrected for the diamagnetism of the sample by the Pascal constant ( $-377 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  per  $\text{Cu}^{2+}$ ) and the Al bag.<sup>13</sup>

20  $\mu\text{m}$  gold wires were attached the single crystal by gold paste. The temperature-dependent conductivity measurements were performed on the best developed surface of the single crystal with a four-probe method on a Quantum Design PPMS 9 system from 2 K to 300 K.

Raman spectra were carried out on a Reinshaw inVia Raman microscope with  $\lambda = 633 \text{ nm}$  at room temperature.

## Results and discussion

We tried to introduce the polymeric coordination anion of Cu-oxalato into an organic-inorganic hybrid and reported an organic-metal  $(\text{BEDT-TTF})_4\text{Cu}(\text{C}_2\text{O}_4)_2$  compound of the 0D anion  $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$ .<sup>6</sup> When  $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{Cu}(\text{C}_2\text{O}_4)_2$  was used as an electrolyte and  $\text{CH}_2\text{Cl}_2$  was used as a solvent, the charge-transfer salt of the 0D  $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$  counteranion was

Table 1 Crystallographic data of 1 and 2

	1	2
Color	Black	Black
Morphology	Plate	Plate
Cell parameters	$a = 8.7710(3) \text{ \AA}$ $b = 17.0116(5) \text{ \AA}$ $c = 20.6017(7) \text{ \AA}$ $\alpha = 104.873(1)^\circ$ $\beta = 102.284(1)^\circ$ $\gamma = 92.349(2)^\circ$ $V = 2888.0(2) \text{ \AA}^3$	$a = 8.7716(3) \text{ \AA}$ $b = 16.9903(6) \text{ \AA}$ $c = 20.5716(7) \text{ \AA}$ $\alpha = 104.794(2)^\circ$ $\beta = 102.209(2)^\circ$ $\gamma = 92.243(1)^\circ$ $V = 2883.2(2) \text{ \AA}^3$
Crystal system	Triclinic	Triclinic
Space group	$P1$	$P1$
Z	2	2
Formula	$\text{C}_{38}\text{H}_{32}\text{Cu}_2\text{O}_{14}\text{S}_12\text{Se}_{12}$	$\text{C}_{38}\text{H}_{32}\text{Cu}_2\text{O}_{14}\text{S}_{24}$
Formula weight	2171.96	1609.16
$F(000)$	2060	1628
$D_{\text{calc}}$ , $\text{g cm}^{-3}$	2.502	1.907
$\mu$ , $\text{mm}^{-1}$	8.808	1.716
$\theta$ , $^\circ$	25.0	25.0
No. total reflns	32181	31941
No. unique reflns ( $R_{\text{int}}$ )	9802(0.1003)	9821(0.0660)
No. obs [ $I \geq 2\sigma(I_0)$ ]	3895	4982
No. params	707	713
$R_1$ , $wR_2$ [ $I \geq 2\sigma(I_0)$ ]	0.0604, 0.1523	0.0464, 0.0881
$R_1$ , $wR_2$ (All data)	0.1752, 0.1910	0.1257, 0.1049
GOF	0.898	0.914
Shift/error	0.000/0.000	0.000/0.000
$\Delta\rho$ , $\text{e \AA}^{-3}$	1.437(−1.168) <sup>a</sup>	0.727(−0.566)
CCDC	870314	836180

<sup>a</sup> Ghost peak of Se.

obtained. When  $(\text{C}_4\text{H}_9)_4\text{N}^+$  was replaced by  $(\text{C}_2\text{H}_5)_3\text{NH}^+$  as an electrolyte and  $\text{C}_6\text{H}_5\text{Cl}$ – $\text{CH}_3\text{OH}$  was used as a solvent, a two-dimensional (6,3) grid Cu-oxalato anion was obtained in the produced crystal.

The single crystal structure of  $\text{BETS}_3[\text{Cu}_2(\text{C}_2\text{O}_4)_3](\text{CH}_3\text{OH})_2$  (1) was determined from X-ray diffraction data. It crystallizes in a triclinic form with cell parameters:  $a = 8.7716(3) \text{ \AA}$ ,  $b = 16.9903(6) \text{ \AA}$ ,  $c = 20.5716(7) \text{ \AA}$ ,  $\alpha = 104.794(2)^\circ$ ,  $\beta = 102.209(2)^\circ$ ,  $\gamma = 92.243(2)^\circ$ ,  $V = 2883.1(2) \text{ \AA}^3$ ,  $Z = 2$ , space group  $P1$  and  $T = 293 \text{ K}$ . When compared to  $(\text{BEDT-TTF})_3[\text{Cu}_2(\text{C}_2\text{O}_4)_3](\text{CH}_3\text{OH})_2$  (2), the  $a$  and  $b$  axis expand by 0.2% and 0.5%, respectively whereas the  $c$  axis expands by 2.3% (Table 1).<sup>6</sup> Each independent unit contains three BETS ( $\text{BETS}_1$ ,  $\text{BETS}_2$ ,  $\text{BETS}_3$ ), three oxalate, two Cu ( $\text{Cu}_1$ ,  $\text{Cu}_2$ ) and two  $\text{CH}_3\text{OH}$  molecules (Fig. 2). One of the C atoms (C20) on the ethylene group is disordered in two positions. Donor layers and two-dimensional honeycomb  $[\text{Cu}_2(\text{C}_2\text{O}_4)_3]^{2-}$  layers are stacked alternatively along the  $c$  axis with hydrogen bonds between the donor and anion (Fig. 3). The right and left inclinations of the molecular planes of BETS are alternately arranged in a 2 : 1 ratio along the  $b$  axis. Donors stack face-to-face to form a donor column along the  $a$  axis. Columns are packed side-by-side to form a donor layer on the  $ac$  plane. The donor arrangement belongs to the  $\theta^{21}$ -phase.<sup>14</sup> There is no weak interaction between the BETS molecules within the column. There are  $\text{S}\cdots\text{S}$ ,  $\text{S}\cdots\text{Se}$  and  $\text{Se}\cdots\text{Se}$  contacts between neighbouring columns, forming a (4,4) grid. There is no  $\text{S}\cdots\text{S}$  contact between  $\text{ET}_2\cdots\text{ET}_2$  and  $\text{ET}_3\cdots\text{ET}_3$  and the  $\text{S}\cdots\text{S}$  contact network

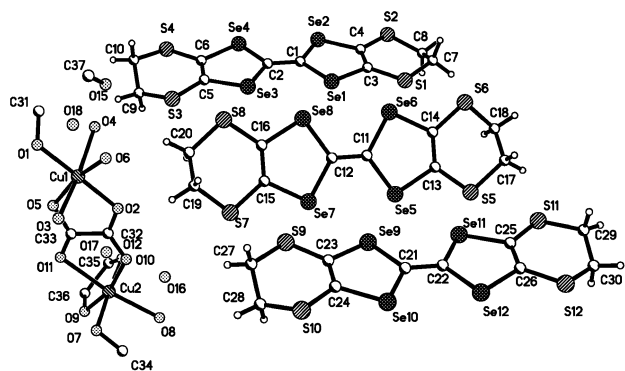


Fig. 2 Atomic scheme of **1** in an independent unit.

is  $(6^2 \cdot 4^1) \cdot (6^2 \cdot 4^2 \cdot 8^2)$  in **2** (Fig. 4). In **1**, the dihedral angles between BETS<sub>1</sub> and BETS<sub>2</sub> or BETS<sub>3</sub> are 123.8–124.1°. In **2**, the dihedral angles between ET1 and ET2 or ET3 are 125–126°. The donor arrangement in **1** is different to the donor arrangements in the charge-transfer salts of the heterometallic honeycomb anion [CrMn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>−</sup><sub>n</sub>: a β-type BEDT-TTF in (BEDT-TTF)<sub>3</sub>[CrMn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sub>x</sub> and an α-type BETS in BETS<sub>3</sub>[CrMn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>](CH<sub>2</sub>Cl<sub>2</sub>)<sub>x</sub>, and in the organic–inorganic hybrid of the OD anion: a β'-type BEDT-TTF in (BEDT-TTF)<sub>4</sub>Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.<sup>6,7</sup>

In **1**, the bond lengths of the TSeF core are listed in Table 2, although there is no suitable function for the formal charge and bond lengths on the charge-transfer complexes of BETS as charge-transfer salts of BEDT-TTF.<sup>15</sup> The  $\delta$  value, which is concluded from the bond lengths of the TSeF core and is sensitive to the formal charge of the organic donor. The  $\delta$

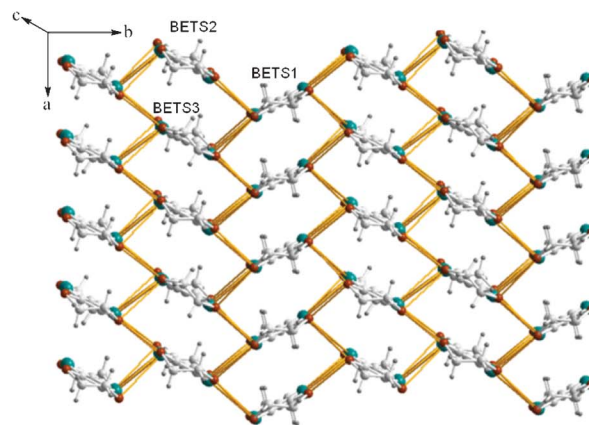


Fig. 4 Donor arrangement viewed along the *c* axis in **1** (top) and **2** (bottom). The solid brown line (**1**) and solid blue line (**2**) are the Se...Se, Se...S and S...S contacts.

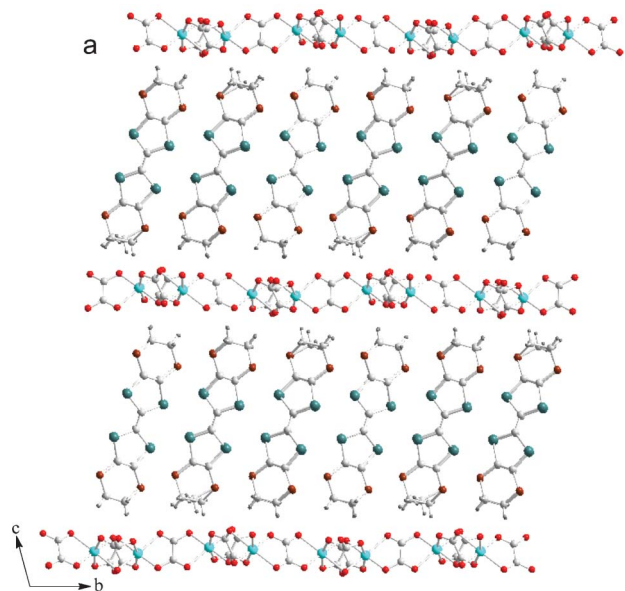


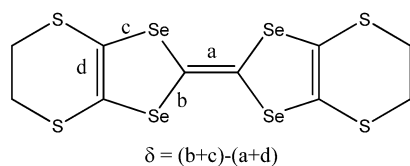
Fig. 3 Crystal structure of **1** without solvent molecules, viewed along the *c* axis. Color code: Cu = blue; O = red; C = white; S = brown; Se = dark-green; H = small white.

value of BETS<sub>1</sub>, BETS<sub>2</sub> and BETS<sub>3</sub> in **1** is smaller than the  $\delta$  value of BETS<sup>0</sup>, and close to the  $\delta$  value of reported charge-transfer salts of BETS<sup>+0.5</sup> (Table 2).<sup>9,16</sup> Therefore, the formal charge should be assigned to a fraction value around +0.5 or higher. In **2**, the formal charge of the BEDT-TTF molecule was assigned to +0.56–0.65 from the bond lengths and the total formal charge of three BEDT-TTF molecules in an independent unit is 1.83 at room temperature (Table 3).

In the two-dimensional honeycomb anion layer, metal atoms were coordinated by six O atoms from the three disubdentate oxalates in the Q<sub>2</sub>(Cu1) and Q<sub>3</sub>(Cu2) Jahn–Teller distortion mode of a CuO<sub>6</sub> octahedron (Fig. 5).<sup>17</sup> Compared with **2**, the O–Cu–O angles between neighboring O atoms and the Cu–O distance in the equatorial plane are in the same range and the Cu–O distances from the direction of the apex are shorter (Table 4). The *trans* O–Cu1–O angle between two O atoms from the apex direction decreases from 162.3(1)° in **2** to 161.5(4)° in **1** while the *trans* O–Cu2–O angle between two O atoms from the apex direction increases from 161.80(4)° in **2** to 163.0(4)° in **1**. Depending on the Cu–O distance, the oxidation state of Cu(1) and Cu(2) is assigned to +1.98 and +2.07 in **1** and +2.11 and +2.14 in **2**.<sup>18</sup> This is in the same range of +2.06–2.15 in the Jahn–Teller distorted three-dimensional copper-oxalate framework [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>Cu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> with an oxidation state of

**Table 2** Bond lengths of the TSeF core in the BETS molecule

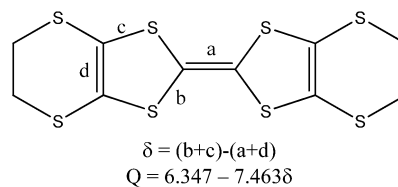
(a-d were defined as follows)



	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	$\delta$
BETS <sup>0</sup>	1.338(7) 1.338(7)	1.916(5) 1.896(5)	1.905(5) 1.906(5)	1.338(8) 1.328(8)	1.15
BETS <sub>1</sub>	1.349(15)	1.893(11) 1.887(11) 1.892(11)	1.891(11) 1.888(11) 1.894(12)	1.360(16) 1.364(14)	1.06
BETS <sub>2</sub>	1.357(16)	1.881(10) 1.870(12) 1.884(11)	1.874(11) 1.889(11) 1.893(11)	1.362(14) 1.348(14)	1.07
BETS <sub>3</sub>	1.347(16)	1.866(11) 1.900(12) 1.900(11)	1.905(11) 1.906(11) 1.903(11)	1.348(14) 1.359(18)	1.08
$\kappa'$ -BETS <sub>2</sub> FeCl <sub>4</sub>	1.349(8)	1.876(10) 1.890(11)	1.896(11) 1.903(11)	1.333(8) 1.335(8)	1.103
$\kappa$ -BETS <sub>2</sub> FeCl <sub>4</sub>	1.358(5)	1.881(6) 1.898(5) 1.875(5)	1.892(5) 1.904(5) 1.906(6)	1.342(5) 1.340(5)	1.084
$\lambda$ -BETS <sub>2</sub> FeCl <sub>4</sub>	1.360(7) 1.370(7)	1.889(6) 1.890(3) 1.884(4)	1.898(5) 1.905(4) 1.893(4)	1.364(7) 1.358(7) 1.343(7)	1.057
$\kappa'$ -BETS <sub>2</sub> Fe(C <sub>2</sub> O <sub>4</sub> )Cl <sub>2</sub>	1.369(6)	1.871(5) 1.890(4) 1.891(5) 1.876(5) 1.872(5) 1.889(4)	1.894(4) 1.892(4) 1.888(5) 1.898(5) 1.892(5) 1.905(5)	1.352(7) 1.337(6)	1.060

+2.<sup>4</sup> The oxidation state of the metal atoms in an independent unit is +4.05 in **1** and +4.25 in **2**. In **2**, the total oxidation state of the donor molecules and metal atoms in an independent unit is +6.08, which is close to +6 to balance the −6 from the three oxalate anions in an independent unit. Therefore, the oxidation state of BETS could be estimated as +0.5–+0.7 in **2**. The Cu1...Cu1 and Cu2...Cu2 distances connected by an oxalate anion are shorter and the Cu1...Cu2 distances connected by an oxalate anion are longer. The disordered CH<sub>3</sub>OH molecules occupy the hexagonal cavity, with hydrogen bonds between the oxalate and solvent molecules. There are C–H...O hydrogen bonds between the donor and anion layer.

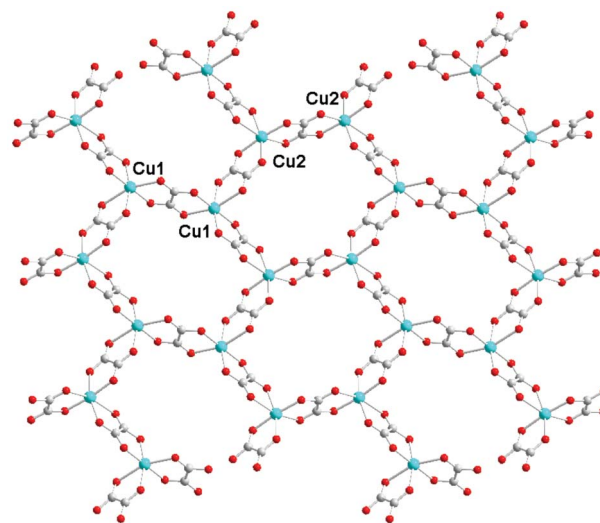
In **1**, an intense band at 1493 cm<sup>−1</sup> was observed in the Raman spectra at room temperature (Fig. 6). This is close to  $\gamma_3$  of BEDT–TTF<sup>+0.5</sup> at 1495 cm<sup>−1</sup> and different from **2** in that an intense band of  $\gamma_3$  was observed at 1477 cm<sup>−1</sup> with a formal

**Table 3** Bond lengths of the TTF core in BEDT–TTF of **2**

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	$\delta$	<i>Q</i>
ET0	1.319	1.746 1.769 1.753	1.757 1.747 1.755	1.335 1.328	0.861	0
ET1	1.366(5)	1.734(5) 1.734(5) 1.737(4)	1.756(4) 1.745(4) 1.747(4)	1.345(6) 1.339(6)	0.776	0.556
ET2	1.371(5)	1.736(5) 1.730(5) 1.728(4)	1.747(4) 1.746(4) 1.741(4)	1.345(6) 1.339(6)	0.766	0.630
ET3	1.376(5)	1.732(5) 1.729(5) 1.730(5)	1.753(4) 1.749(4) 1.753(4)	1.342(6) 1.339(6)	0.764	0.645
Total		1.726(4) 1.736(5)	1.744(4) 1.759(4)			1.831

charge of BEDT–TTF<sup>+0.66</sup>.<sup>19</sup> In the neutral BETS crystal, two intense bands (1493 cm<sup>−1</sup>, 1507 cm<sup>−1</sup>) and one weak band (1530 cm<sup>−1</sup>) were observed in the Raman spectra. This confirms the charge transfer from the BETS molecules to the anion. The formal charge of BETS should be higher than +0.5 due to the difference between Se and S.

The conductivity measurements of **1** were performed with a four-probe method from 2 K to 300 K (Fig. 7). The room temperature conductivity 140 S cm<sup>−1</sup> belongs to a metal of a molecular crystal. The conductivity increased from 300 K to

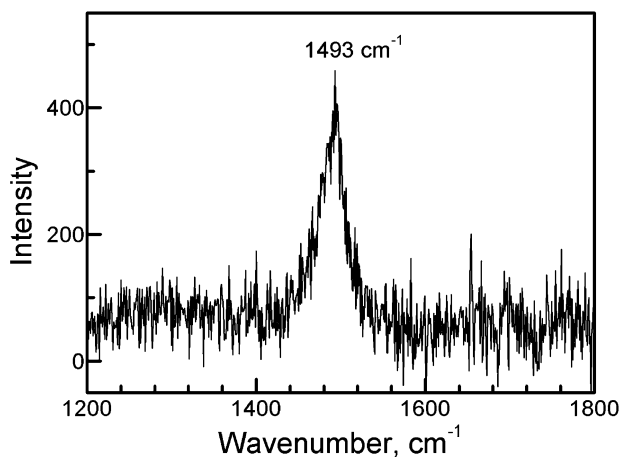
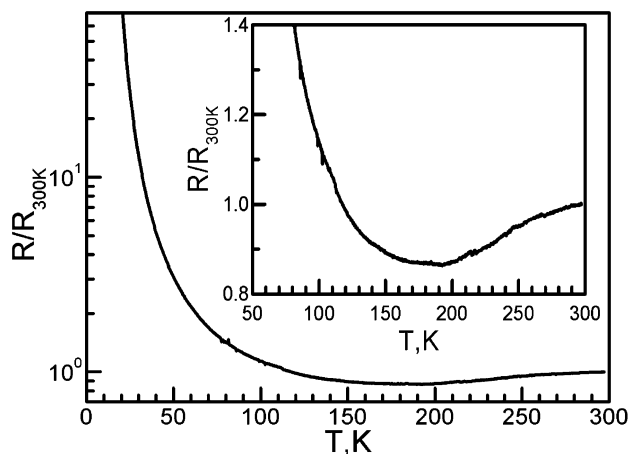
**Fig. 5** Anion layer in the *ab* plane in **1**.

**Table 4** Bond distances (*r*) in the octahedral CuO<sub>6</sub> unit of **1** and **2**

Compound (atom)	<i>r</i>	<i>Q</i>
<b>1</b> (Cu1)	1.953(8), 2.001(9), 2.053(10) 2.072(11), 2.222(8), 2.395(12)	1.98
<b>1</b> (Cu2)	1.971(8), 1.990(9), 1.997(11) 2.007(11), 2.253(10), 2.369(12)	2.08
<b>2</b> (Cu1)	1.949(3), 1.970(3), 1.995(3) 2.018(3), 2.243(3), 2.423(4)	2.11
<b>2</b> (Cu2)	1.949(3), 1.959(3), 1.977(3) 2.000(3), 2.267(3), 2.458(3)	2.14
[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH] <sub>2</sub> Cu <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> Cu1	1.985(2), 1.993(2), 2.064(2) 2.083(2), 2.149(2), 2.201(2)	2.08
[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH] <sub>2</sub> Cu <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> Cu2	1.974(2), 1.988(2), 2.070(2) 2.086(2), 2.170(2), 2.202(2)	2.07

180 K with the metallic behaviour, remained almost constant from 180 K to 150 K and then decreased slowly while cooling and reached 10 S cm<sup>-1</sup> at 17 K. Below 17 K, the resistance increased quickly and the material became insulating at 12 K. The room temperature conductivity is higher than 4 S cm<sup>-1</sup> in **2** and 50 S cm<sup>-1</sup> in θ<sup>21</sup>-(BEDT-TTF)<sub>3</sub>Ag<sub>6.4</sub>I<sub>8</sub>.<sup>8,20</sup> This is different to the reported isostructural compounds of BEDT-TTF and BETS. For example, κ-(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br is a superconductor at 11.6 K, κ-BETS<sub>2</sub>[Cu[N(CN)<sub>2</sub>]Br remains metallic to 4 K and they show the same conductive behaviour above 11.6 K.<sup>9</sup>

In order to compare the conductivity difference between **1** and **2**, the band structures were calculated using a tight-binding approach from the transfer integrals obtained by the extended Hückel method.<sup>21</sup> The formal charge of the BETS molecule is +0.66. The definitions of the overlap integrals between the highest occupied molecular orbitals (HOMOs) on adjacent donor molecules and their values are given in Table 5. The overlap integral in **1** is almost twice that of **2** and the band dispersion in **1** is stronger than in **2**, so an electron exists on the Fermi surface in **1**. This is consistent with the higher room temperature conductivity of **1** (Fig. 8).

**Fig. 6** Raman spectrum of **1** with λ = 633 nm.**Fig. 7** Normalized temperature-dependent resistance of **1**, inset: magnification of the range 50–300 K.

Magnetization measurements were performed on a polycrystalline sample of **1**. At 300 K, the χT value of 0.490 cm<sup>3</sup> K mol<sup>-1</sup> at 1 kOe (Fig. 9) is larger than the value expected for an isolated, spin-only Cu<sup>2+</sup> with S = 1/2 (0.375 cm<sup>3</sup> K mol<sup>-1</sup>) but is similar to the previously reported value.<sup>22</sup> The χT value decreased with decreasing temperature and reached 0.03 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. The susceptibility above 20 K fits the Curie-Weiss law, giving Curie and Weiss constants of C = 0.705(2) cm<sup>3</sup> mol<sup>-1</sup>, θ = -126.8(6) K and R = 5.54 × 10<sup>-5</sup>. The negative Weiss constant suggests an antiferromagnetic inter-

**Table 5** Overlap integrals multiplied by 1000 for **1** and **2**

	<b>1</b>	<b>2</b>
<i>t</i> <sub>1</sub>	-17.20	-7.81
<i>t</i> <sub>2</sub>	8.53	4.34
<i>t</i> <sub>3</sub>	-14.93	-7.05
<i>t</i> <sub>4</sub>	7.59	5.02
<i>t</i> <sub>5</sub>	-9.14	-5.03
<i>t</i> <sub>6</sub>	-7.10	-3.13
<i>t</i> <sub>7</sub>	15.69	6.87
<i>t</i> <sub>8</sub>	18.12	10.08
<i>t</i> <sub>9</sub>	27.78	14.01
<i>t</i> <sub>10</sub>	-14.01	-7.24
<i>t</i> <sub>11</sub>	30.90	18.78



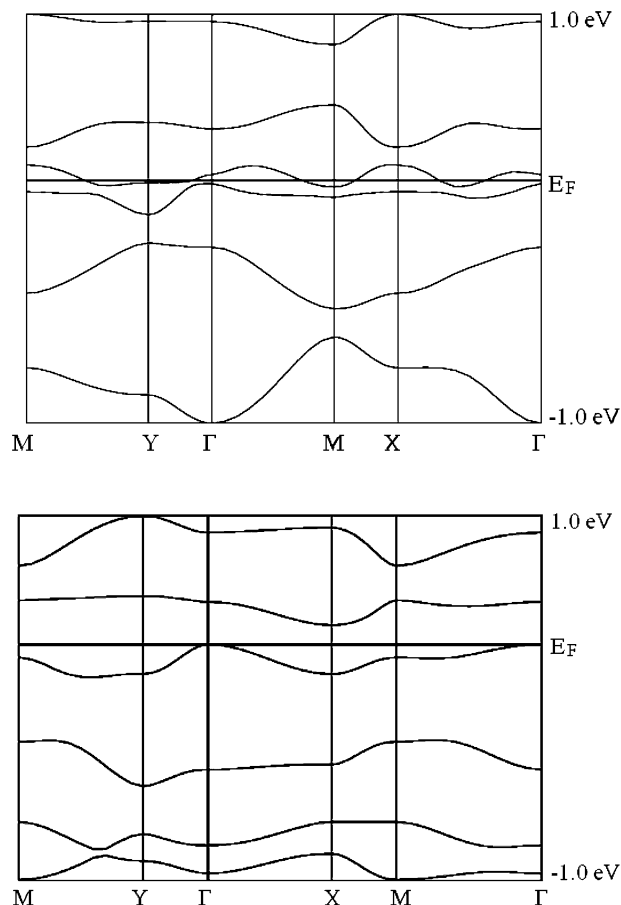


Fig. 8 Band structures of **1** (top) and **2** (bottom).

action between the Cu(II) atoms through the oxalate bridge. It is stronger than  $-29.8(7)$  K in **2** and in the same range of  $-131(7)$  K for  $[(C_2H_5)_3NH]_2Cu_2(C_2O_4)_3$ .<sup>4</sup> The stronger antiferromagnetic interaction may be explained by the difference between the *trans* O–Cu–O angles from the apex direction in

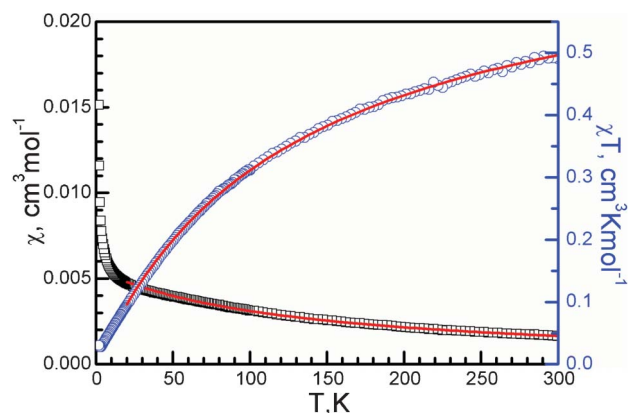


Fig. 9  $\chi$  vs.  $T$  (empty black square),  $\chi T$  vs.  $T$  (empty blue circle) plots of **1**. The red solid lines are fits to the Curie–Weiss law.

the  $CuO_6$  octahedral. The bigger the difference, the stronger the antiferromagnetic interaction observed in  $[(C_2H_5)_3NH]_2Cu_2(C_2O_4)_3$ .<sup>4</sup> At 2 K, the isothermal magnetization of **1** increased with an increasing field and reached  $0.075 N\beta$  at 65 kOe. This is in the same range of  $0.077 N\beta$  at 65 kOe for **2** and  $0.06 N\beta$  at 65 kOe for the 0D antiferromagnetic compound  $CuCl_2(1,4\text{-dioxane})(H_2O)_2$ . This is higher than  $0.04 N\beta$  at 65 kOe for the 1D antiferromagnetic compound  $CuCl_2(1,4\text{-dioxane})(H_2O)_2$  and  $0.0387 N\beta$  in  $[(C_2H_5)_3NH]_2Cu_2(C_2O_4)_3$  at 65 kOe and is lower than  $0.33 N\beta$  at 65 kOe for the 2D antiferromagnetic compound  $(CuCl_2)_3(1,4\text{-dioxane})_2$ .<sup>4,23</sup>

## Conclusions

Metallic conductivity appeared when BEDT–TTF was replaced by BETS in a given structure. The antiferromagnetic interactions between the metal atoms in the Jahn–Teller distorted  $[Cu_2(C_2O_4)_3]^{2-}_n$  layer was enhanced. This material will not only offer a means to develop new molecule-based magnetic conductors but may also provide ways to simulate a magnetic layer that is a crucial requirement for achieving high-temperature superconductivity and giant magnetoresistance in molecular systems for the future. Such work is in progress.

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