



## Article

# First Molecular Superconductor with the Tris(Oxalato)Aluminate Anion, $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·C<sub>6</sub>H<sub>5</sub>Br, and Isostructural Tris(Oxalato)Cobaltate and Tris(Oxalato)Ruthenate Radical Cation Salts

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**Abstract:** Peter Day's research group reported the first molecular superconductor containing paramagnetic metal ions in 1995,  $\beta''$ -(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. Subsequent research has produced a multitude of BEDT-TTF-tris(oxalato)metallate salts with a variety of structures and properties, including 32 superconductors to date. We present here the synthesis, crystal structure, and conducting properties of the newest additions to the Day series including the first superconductor incorporating the diamagnetic tris(oxalato)aluminate anion,  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·C<sub>6</sub>H<sub>5</sub>Br, which has a superconducting T<sub>c</sub> of ~2.5 K.  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·C<sub>6</sub>H<sub>5</sub>Br represents the first example of a  $\beta''$  phase for the tris(oxalato)cobaltate anion, but this salt does not show superconductivity.

**Keywords:** molecular conductor; superconductor; metal; semiconductor; BEDT-TTF; tris(oxalato)metallate

## 1. Introduction

The first paramagnetic superconductor,  $\beta''$ -(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 by the group of Professor Peter Day at the Royal Institution of Great Britain [1]. The ability of tris(oxalato)metallate(III) anions, M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3−</sup>, to bridge through oxalate ions with monocations or metal(II) ions and form 2D sheets opened the door to a huge variety of structures and properties in radical cation salts with BEDT-TTF [2]. This family of salts includes not only paramagnetic superconductors, but also a ferromagnetic metal [3], antiferromagnetic semiconductor [4], and proton conductor [5,6].

Most of the reported salts in the BEDT-TTF-tris(oxalato)metallate family are 4:1 salts having the formula (BEDT-TTF)<sub>4</sub>(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·G. The lattice consists of cation layers of BEDT-TTF alternating with anion layers where hydrogen bonding between the terminal ethylene groups of BEDT-TTF and the anion layer determine the donor molecule packing arrangement. The anion layers are built up of M and A bridged by oxalate ligands to form a honeycomb with guest molecules, G, contained within the hexagons.

The most widely studied 4:1 salts in this “Day series” are the  $\beta''$  salts, which crystallise in the monoclinic C2/c space group, of which 32 are superconductors [1,2,7–30]. The counter cation (A = H<sub>3</sub>O<sup>+</sup>/K<sup>+</sup>/NH<sub>4</sub><sup>+</sup>/Rb<sup>+</sup>) and the tris(oxalato)metallate metal centre can be changed (M = Fe [1,7–19,25], Cr [20–25], Co [25], Al [25], Mn [17,26], Ga [24,27,28] Ru [29], Rh [30]), which has a small effect on the electrical properties of the material owing to the change in size of A and M. For example,  $\beta''$ -(BEDT-TTF)<sub>4</sub>(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·G,

where **G** = benzonitrile, sees a reduction of superconducting  $T_c$  to 5.5–6.0 K when **M** = Cr, compared to when **M** = Fe 7.0–8.5 K. A more marked effect on the electrical properties and the superconducting  $T_c$  [31] is observed when changing the guest molecule, **G**—the solvent used for the electrocrystallization. Changing **G** from benzonitrile to different sized and shaped guest molecules can alter the conducting properties from superconducting to metallic or semiconducting [2,7–30]. The highest superconducting  $T_c$  values are obtained when longer guest solvent molecules are used, which increase the *b* axis length the furthest, e.g., **G** = benzonitrile, nitrobenzene [31].

When **G** = benzonitrile, crystals of an additional 4:1 orthorhombic phase are also obtained when **M** = Fe or Cr. Crystals of this 4:1 orthorhombic phase are the only phase obtained with **G** = benzonitrile when **M** = Co [25], Al [25], or Rh [30], and the  $\beta''$  phase has not been reported. This semiconducting phase crystallises in the orthorhombic space group *Pbcn* with a pseudo- $\kappa$  donor packing. (BEDT-TTF<sup>+</sup>)<sub>2</sub> dimers are surrounded by neutral BEDT-TTF<sup>0</sup> monomers. The  $\text{C}\equiv\text{N}$  group of benzonitrile is disordered over two positions directed towards **A**, rather than along the *b* axis towards **M**, as seen in the  $\beta''$  salts. The chirality of the tris(oxalato)metallates in the anion layers differs between the  $\beta''$  and pseudo- $\kappa$  salts despite both having an overall racemic lattice. In the  $\beta''$  salts, each anion layer contains only a single enantiomer of  $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$  with alternating layers being of the opposing enantiomer. However, in the pseudo- $\kappa$  salts, each anion layer is identical with alternating rows of  $\Delta$  or  $\Lambda$  enantiomers.

When **G** is too large to fit inside the honeycomb cavity of the anion layer, a 4:1 triclinic phase is obtained. The guest molecule in these salts protrudes on one side of the anion layer and not on the other. The two different faces of the anion layer then lead to two different packing modes of the donor layer within the same crystal, e.g., both  $\alpha$  and  $\beta''$  donor packing (**G** = PhCH<sub>2</sub>CN, PhN(CH<sub>3</sub>)CHO, PhCOCH<sub>3</sub>, or PhCH(OH)CH<sub>3</sub>) [32] or  $\alpha$  and pseudo- $\kappa$  (**G** = 1,2-Br<sub>2</sub>Ph) [33]. An  $\alpha$ - $\beta''$  salt has also been obtained with the inclusion of a chiral guest molecule (**G** = *sec*-phenethyl alcohol, PhCH(OH)CH<sub>3</sub>) in both the chiral *S* form and the racemic *R/S* form. A small difference in the metal–insulator transition temperature is observed between the racemic and the chiral salts owing to the disorder, which is found only in the racemate [34].

While the 4:1 salts make up the majority of BEDT-TTF-tris(oxalato)metallate salts, some semiconducting 3:1 salts have been obtained when using smaller guest molecules (**G** = DMF, acetonitrile, dichloromethane, nitromethane; cation = Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>; metal = Fe [35], Cr [36–39], Al [39]). A 2:1 salt has also been reported in which an 18-crown-6 molecule is the guest in the honeycomb cavity,  $\beta''$ -(BEDT-TTF)<sub>2</sub>[(H<sub>2</sub>O)(NH<sub>4</sub>)<sub>2</sub>M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].18-crown-6 (**M** = Cr, Rh, Ru, Ir). Both the Cr and Rh salts show a bulk Berezinskii–Kosterlitz–Thouless superconducting transition [40–42]. Changing the counter cation **A** has produced several salts where the packing of the anion layer differs from the aforementioned honeycomb packing arrangement giving salts  $\beta'$ -(BEDT-TTF)<sub>5</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].(H<sub>2</sub>O)<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub> [43] (**A** = tetraethylammonium),  $\eta$ -(BEDT-TTF)<sub>4</sub>(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> [35] (**A** = lithium),  $\alpha'''$ -(BEDT-TTF)<sub>9</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>8</sub>Na<sub>18</sub>(H<sub>2</sub>O)<sub>24</sub> [44,45] (**A** = sodium),  $\alpha$ -(BEDT-TTF)<sub>10</sub>(18-crown-6)<sub>6</sub>K<sub>6</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>4</sub>(H<sub>2</sub>O)<sub>24</sub> [45] (**A** = potassium), and  $\alpha$ -(BEDT-TTF)<sub>12</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>.(H<sub>2</sub>O)<sub>*n*</sub> [46] (**A** = potassium or caesium, *n* = 15 or 16). Changing the **M**(III) to Ge(IV) produces very different structures in the semiconductors (BEDT-TTF)<sub>2</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].PhCN [47], (BEDT-TTF)<sub>5</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub> [48], (BEDT-TTF)<sub>7</sub>[Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.87</sub>(H<sub>2</sub>O)<sub>0.09</sub> [48], and (BEDT-TTF)<sub>4</sub>Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.50</sub> [49].

We report here the synthesis, crystal structures, and conducting properties of the first superconductor incorporating the tris(oxalato)aluminate anion,  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.C<sub>6</sub>H<sub>5</sub>Br ( $T_c \sim 2.5$  K), the first example of a  $\beta''$  phase for the tris(oxalato)cobaltate anion (**G** = PhBr), and two new  $\beta''$  salts from tris(oxalato)ruthenate (**G** = PhCl or PhF). Resistivity is also presented for  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)Ru(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.PhBr, which shows a superconducting  $T_c$  of 2.8 K, though the crystals were very thin and not suitable for a publishable X-ray dataset.

## 2. Results and Discussion

All salts  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·G (M-G = Al-PhBr, Co-PhBr, Ru-PhCl, Ru-PhF) are isostructural with the previously reported Day series  $\beta''$ -(BEDT-TTF)<sub>4</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·G. Ru-PhBr is also isostructural, though the crystals were very thin and not suitable for a publishable X-ray dataset. They crystallise in the monoclinic space group C2/c. The asymmetric unit contains two crystallographically independent BEDT-TTF molecules, half an M(C<sub>2</sub>O<sub>4</sub>)<sup>3−</sup> molecule, half a guest halobenzene molecule, and half a H<sub>3</sub>O<sup>+</sup> molecule (Table 1). The long-range structure consists of ordered alternating layers of BEDT-TTF donor molecules and M(C<sub>2</sub>O<sub>4</sub>)<sup>3−</sup> anions (Figure 1). The two crystallographically independent donor BEDT-TTF molecules form two-dimensional stacks along the *a/b* crystallographic axis in a  $\beta''$  arrangement (Figure 2). A number of predominately side-to-side sulphur-sulphur interactions below the sum of the van der Waals radii are present (Table 2). The estimated charge on BEDT-TTF cations can be calculated via the method of Guionneau et al. [50] from the central C=C and C-S bond lengths of the TTF core and results in a charge of approximately +0.5 for each BEDT-TTF molecule, as expected (Table 3).

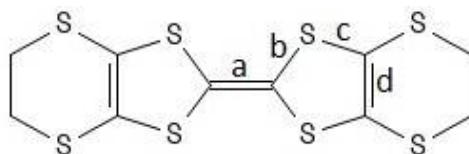
**Table 1.** Crystal data for  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·G salts.

Salt	Al-PhBr 290 K	Al-PhBr 110 K	Co-PhBr 150 K	Ru-PhF 293 K	Ru-PhCl 298 K
Formula	C <sub>52</sub> H <sub>40</sub> AlBrO <sub>13</sub> S <sub>32</sub>	C <sub>52</sub> H <sub>40</sub> AlBrO <sub>13</sub> S <sub>32</sub>	C <sub>52</sub> H <sub>40</sub> BrCoO <sub>13</sub> S <sub>32</sub>	C <sub>52</sub> H <sub>40</sub> FO <sub>13</sub> RuS <sub>32</sub>	C <sub>52</sub> H <sub>40</sub> O <sub>13</sub> S <sub>32</sub> ClRu
Fw (g mol <sup>−1</sup> )	2005.65	2005.65	2037.60	2018.83	2035.28
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
Z	4	4	4	4	4
T (K)	290 (2)	110 (2)	150 (2)	293 (2)	293 (2)
<i>a</i> (Å)	10.2851 (2)	10.2520 (3)	10.2306 (3)	10.32786 (19)	10.32017 (19)
<i>b</i> (Å)	19.9472 (4)	19.7919 (7)	19.7508 (5)	19.9521 (4)	20.0264 (4)
<i>c</i> (Å)	35.597 (3)	35.4275 (11)	35.2520 (9)	34.9966 (6)	35.161 (3)
$\alpha$ (°)	90	90	90	90	90
$\beta$ (°)	93.399 (7)	93.843 (7)	93.938 (7)	93.010 (7)	93.586 (7)
$\gamma$ (°)	90	90	90	90	90
Volume (Å <sup>3</sup> )	7290.1 (6)	7172.3 (4)	7106.3 (3)	7201.5 (2)	7252.6 (6)
Density (g cm <sup>−3</sup> )	1.827	1.857	1.905	1.862	1.864
$\mu$ (mm <sup>−1</sup> )	1.553	1.578	1.806	1.209	1.235
<i>R</i> <sub>1</sub>	0.0547	0.0688	0.0431	0.0460	0.0442
<i>wR</i> (all data)	0.1401	0.1526	0.0914	0.318	0.1089

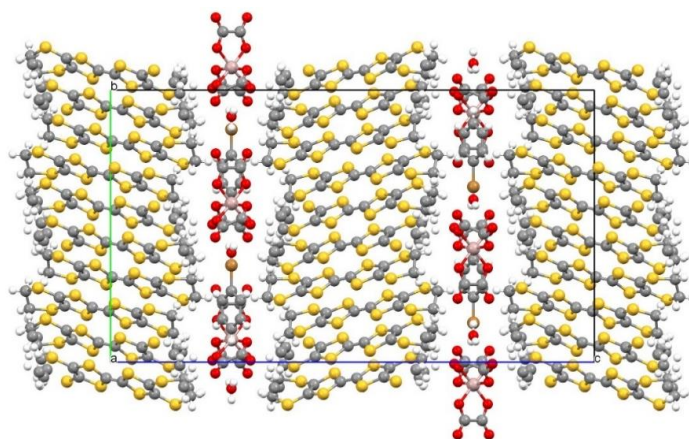
**Table 2.** S ... S close contacts below the van der Waals distance in  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·G salts.

Contact (Å)	Al-PhBr 290 K	Al-PhBr 110 K	Co-PhBr 150 K	Ru-PhF 293 K	Ru-PhCl 298 K
S1 ... S7	3.4069 (13)	3.3795 (19)	3.3683 (11)	3.4015 (14)	3.4283 (11)
S3 ... S7	3.5046 (13)	3.458 (2)	3.4544 (11)	3.5369 (15)	3.5290 (11)
S2 ... S9	3.3138 (14)	3.2838 (19)	3.2864 (11)	3.3744 (15)	3.3528 (11)
S2 ... S11	3.3720 (13)	3.340 (2)	3.3413 (11)	3.3954 (15)	3.3842 (11)
S6 ... S15	3.5231 (14)	3.463 (2)	3.4475 (12)	3.5236 (17)	3.5190 (13)
S8 ... S15	3.5704 (15)	3.502 (2)	3.4904 (13)	3.6182 (17)	3.5869 (12)
S8 ... S10	3.5889 (14)	3.550 (2)	3.5551 (13)	3.6169 (16)	3.6031 (13)

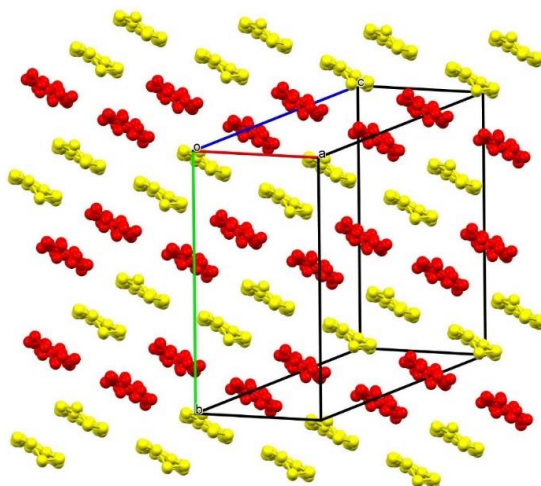
**Table 3.** Average bond lengths (Å) in BEDT-TTF molecules with approximation of the charge on the molecules.  $\delta = (b + c) - (a + d)$ ,  $Q = 6.347 - 7.463\delta$  [50].



Salt	Donor	a	b	c	d	$\delta$	Q
Al-PhBr 290 K	A	1.376	1.73925	1.7515	1.352	0.763	0.65
	B	1.373	1.74025	1.753	1.347	0.773	0.58
Al-PhBr 110 K	A	1.364	1.74475	1.75675	1.346	0.792	0.44
	B	1.376	1.7435	1.75725	1.3455	0.779	0.53
Co-PhBr 150 K	A	1.367	1.73775	1.75275	1.345	0.779	0.54
	B	1.369	1.738	1.7515	1.346	0.775	0.57
Ru-PhF 293 K	A	1.36	1.7385	1.74475	1.349	0.774	0.57
	B	1.367	1.73325	1.74525	1.354	0.758	0.69
Ru-PhCl 298 K	A	1.366	1.737	1.7475	1.349	0.770	0.60
	B	1.366	1.73575	1.74625	1.349	0.767	0.62

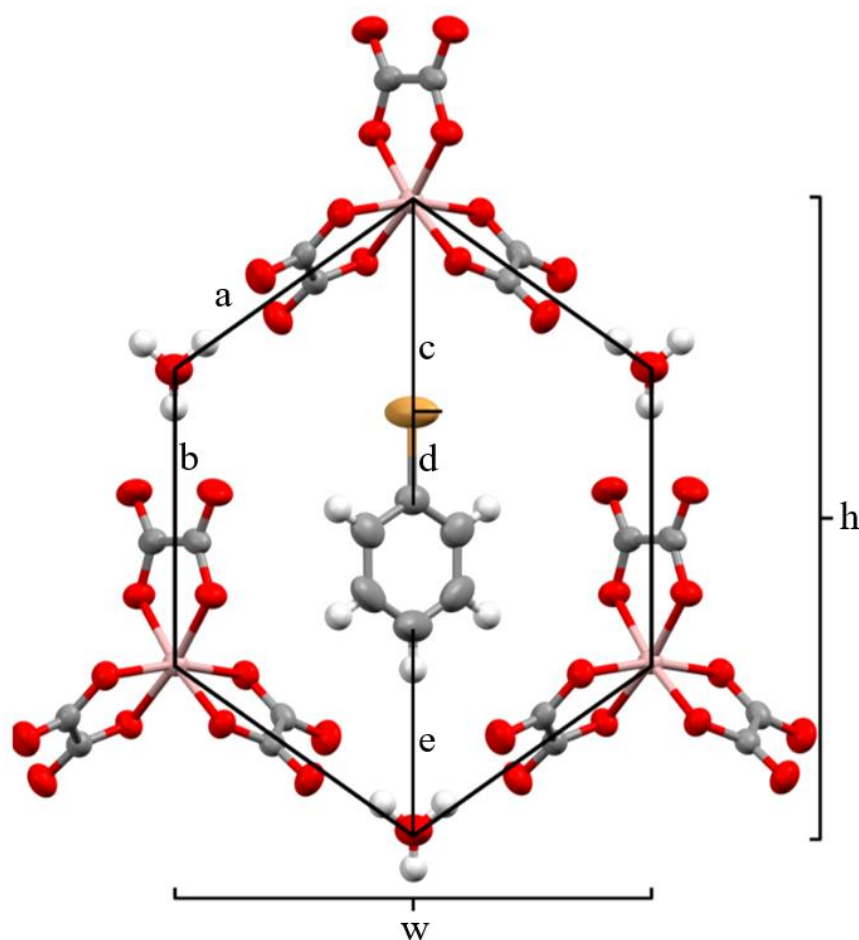


**Figure 1.** Layered structure of Al-PhBr. The other salts reported in this paper are isostructural. Carbon atoms are grey, hydrogen atoms white, oxygen atoms red, sulphur atoms yellow, aluminium atoms pink, and bromine atoms brown. The  $b$  axis is shown in green, and the  $c$  axis is shown in blue.



**Figure 2.**  $\beta''$  BEDT-TTF layer packing in Al-PhBr. The other salts reported in this paper are isostructural. The two crystallographically independent BEDT-TTF molecules are shown in different colours. Hydrogens have been removed for clarity. The  $a$  axis is shown in red, the  $b$  axis in green, and the  $c$  axis in blue.

The anion layer consists of a honeycomb arrangement of  $M(C_2O_4)^{3-}$ , perpendicular to the long axis of the BEDT-TTF molecules, resulting in a hexagonal cavity that is occupied by the guest halobenzene molecule. Each anion layer contains a single enantiomer of the tris(oxalato)metallate ion with adjacent layers containing the alternate enantiomer, which gives an overall racemic lattice. The hexagonal cavity and the orientation of the guest halobenzene molecule within it are shown in Figure 3 and Table 4. Distances  $a$ ,  $b$ ,  $h$ , and  $w$  represent the dimensions of the hexagonal cavity. The latter two are the height and width of the cavity, respectively, and  $\delta$  is the angle of the benzene ring plane relative to the plane of the hexagonal cavity (measured as the least-squares plane of the three metal atoms making up three corners of the hexagon). For  $M = Rh$ , we see a reduction in height ( $h$ ) of the hexagonal cavity going from  $G = PhCl$  to the smaller  $PhF$ , accompanied by a reduction in the length of the  $b$  axis of the unit cell. For salt **Al-PhBr**, we observed a  $T_c$  of  $\sim 2.5$  K (Figure 4), which is similar to previously published salts of  $\beta''$ -(BEDT-TTF) $_4[(H_3O)M(C_2O_4)_3] \cdot G$ , where  $G =$  bromobenzene. When applying a magnetic field along the  $c^*$  axis, the critical field of the superconductivity at 0.7 K is about 0.2 T. This is comparable to other salts in the Day series, for example: the Fe-DMF salt has a  $T_c$  of 2.0 K, and  $H_{c2}$  in a perpendicular field is  $\sim 0.1$  T [51]. Higher  $T_c$  salts in the Day series have higher  $H_{c2}$  values (2–5 T) [52], and these quasi-2D superconductors are strongly anisotropic [53].

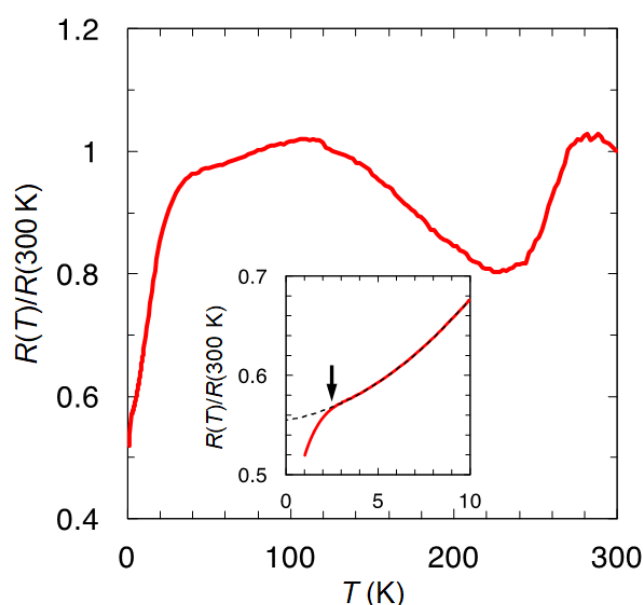


**Figure 3.** Honeycomb cavity in the anion layer of  $\beta''$ -(BEDT-TTF) $_4(H_3O)M(C_2O_4)_3 \cdot G$  salts with measurement parameters labelled ( $a$ – $e$ ,  $w$  = width,  $h$  = height). Carbon atoms are grey, hydrogen atoms white, and oxygen atoms red. This image shows salt **Al-PhBr**, where aluminium atoms are pink and bromine atoms brown.



**Table 4.** Honeycomb cavity measurements in the anion layer (see Figure 3) of  $\beta''$ -(BEDT-TTF)<sub>4</sub>(H<sub>3</sub>O)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·G salts.

Salt Temp.	Al-PhBr 290 K	Al-PhBr 110 K	Co-PhBr 150 K	Ru-PhF 293 K	Ru-PhCl 298 K
Distances (Å)					
<i>a</i>	6.269 (3)	6.255 (6)	6.249 (3)	6.292 (3)	6.312 (2)
<i>b</i>	6.387 (5)	6.111 (10)	6.286 (6)	6.380 (5)	6.377 (4)
<i>c</i>	4.5360 (16)	4.487 (3)	4.5212 (10)	4.804 (13)	4.331 (16)
<i>d</i>	1.894 (6)	1.905 (10)	1.902 (6)	1.377 (14)	1.737 (6)
<i>e</i>	4.401 (9)	4.338 (19)	4.296 (10)	4.786 (13)	4.543 (9)
<i>h</i>	13.560 (5)	13.481 (10)	13.464 (6)	13.572 (5)	13.649 (4)
<i>w</i>	10.2851 (2)	10.2520 (3)	10.2306 (3)	10.32786 (19)	10.32017 (19)
O4-cation	3.066 (5)	3.004 (11)	2.985 (6)	2.956 (6)	2.962 (5)
O6-cation	2.857 (3)	2.851 (6)	2.842 (3)	2.846 (6)	2.831 (3)
O1-cation	3.083 (5)	3.073 (9)	3.112 (5)	2.941 (5)	2.996 (4)
Angles (°)					
$\delta$	33.522 (3)	33.378 (3)	33.60 (13)	33.74 (19)	32.677 (3)

**Figure 4.** Electrical resistivity for Al-PhBr.

The Al<sup>3+</sup> ion of tris(oxalato)aluminate is smaller than previous examples, where **M** = Fe [13,17], Ga [28], Rh [30], and Ru [29] ( $T_c$  = ~3.8, ~3.0, ~2.9, ~2.8 K, respectively, for **G** = bromobenzene), and the  $T_c$  is smaller for **M** = Al at ~2.5 K. A comparison of the *b* axis length of these bromobenzene salts at room temperature showed that the **M** = Fe salt has the longest at 20.0546(15) Å and also the highest ~3.8 K [13,17]; **M** = Rh has an intermediate *b* axis of 20.0458(4) Å and a  $T_c$  of ~2.9 K [30]; while **M** = Al has the shortest *b* axis of 19.9472(4) Å and the lowest  $T_c$  at ~2.5 K. A direct comparison with the **M** = Ga [28] and Ru [29] salts cannot be made owing to **A** = K<sub>x</sub>(H<sub>3</sub>O)<sub>1-x</sub> rather than H<sub>3</sub>O for these salts. Salts with **M** = Cr [23] and Mn [17] have been reported with  $T_c$ s of 1.5 K and 2.0 K, respectively, but crystal structures are not published for the comparison of the *b* axes. Our crystals of Co-PhBr did not show superconductivity (Figure 5), with the *b* axis of this salt being much shorter than all other PhBr salts at 19.7508(5) Å.

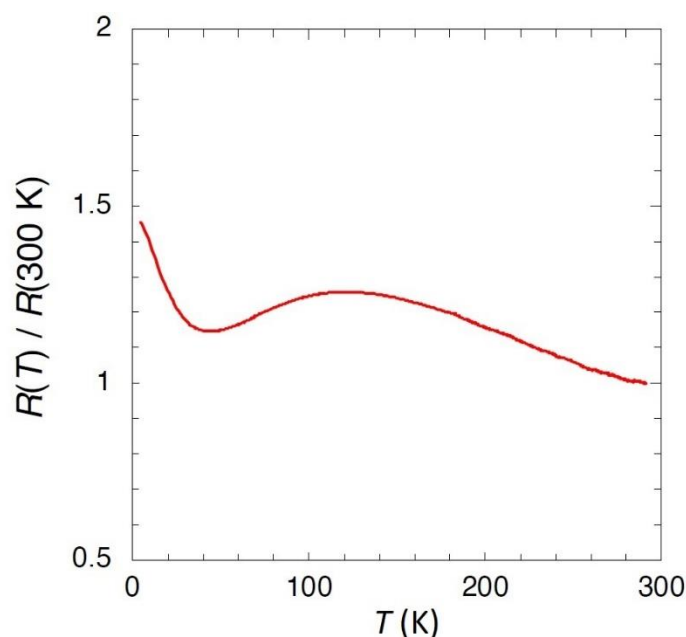
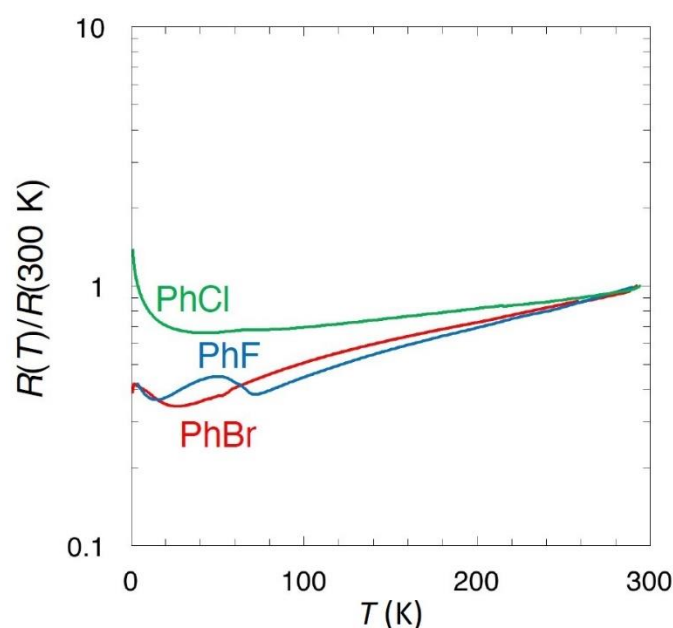


Figure 5. Electrical resistivity for Co-PhBr.

There are thirty-two superconductors to date having the formula  $\beta''\text{-(BEDT-TTF)}_4[(\text{A})\text{M}(\text{C}_2\text{O}_4)_3]\cdot\text{G}$  ( $\text{M} = \text{Fe, Cr, Ga, Rh, Ru, Mn}$ ,  $\text{G} = \text{guest molecule}$ ,  $\text{A} = \text{H}_3\text{O}^+/\text{K}^+/\text{NH}_4^+$ ) [1,2,7–30]. There is negligible  $\pi$ -d interaction in  $\beta''\text{-(BEDT-TTF)}_4[(\text{A})\text{M}(\text{C}_2\text{O}_4)_3]\cdot\text{G}$  salts because the  $\text{M}^{3+}$  ions are located in the centre of the anion layer, distant from the BEDT-TTF layer (Figure 1). This is confirmed by the similar  $T_c$ s that are observed for isostructural salts with the same  $\text{A}$  and  $\text{G}$ , but which differ only in the presence of paramagnetic  $\text{Fe}^{3+}$  ( $S = 5/2$ ) or non-magnetic  $\text{Ga}^{3+}$  [53,54]. A much more marked effect on the value of  $T_c$  is observed when changing the guest molecule,  $\text{G}$ . Changing  $\text{M}$  and  $\text{G}$  leads to a change in the length of the unit cell dimensions. A correlation between the  $b$  axis length and superconducting  $T_c$  has been observed through structural analysis [31]. The effect of chemical pressure through changing  $\text{G}$  and  $\text{M}$  is mainly attributed to the guest molecule,  $\text{G}$ , which is oriented with the R-group oriented in the  $b$  direction (Figure 3). The longest molecules, benzonitrile and nitrobenzene, have the highest  $T_c$ s observed in the family, and the relationship between  $T_c$  and the guest molecule size can be observed in the series of salts with halobenzene guest molecules [31]. Only the higher  $T_c$  salts in this family show insulating behaviour just above  $T_c$  owing to charge disproportionation in these salts [55–58].

Figure 6 shows the resistivity of  $\beta''\text{-(BEDT-TTF)}_4(\text{H}_3\text{O})\text{Ru}(\text{C}_2\text{O}_4)_3\cdot\text{G}$ , where  $\text{G} = \text{PhBr, PhCl, or PhF}$ . **Ru-PhBr** for  $\text{A} = \text{K}_x(\text{H}_3\text{O})_{1-x}$  has previously been studied by Prokhorova et al. [29] with a sample-dependent  $T_c$  in the range 2.8–6.3 K. Resistivity measurements on our crystals of  $\beta''\text{-(BEDT-TTF)}_4(\text{H}_3\text{O})\text{Ru}(\text{C}_2\text{O}_4)_3\cdot\text{PhBr}$  gave a  $T_c$  of 2.8 K, which was as expected based on the  $b$  axis length [31]. Upon reducing the size of  $\text{G}$  from PhBr to PhCl or PhF, no superconductivity was observed. Both **Ru-PhCl** and **Ru-PhF** showed semiconducting behaviour (Figure 6). Both **Ru-PhCl** and **Ru-PhF** had shorter  $b$  axis lengths compared to the Ru-PhBr salt. However, the  $b$  axis lengths in semiconducting **Ru-PhCl** and **Ru-PhF** were longer than that in superconducting **Al-PhBr** (Table 3). This indicates that other factors, such as the shape and the electric dipole of the guest molecule, may have minor influences even though the  $b$  axis length predominantly affects the electronic state, including the  $T_c$  [31].



**Figure 6.** Electrical resistivity for  $\beta''$ -(BEDT-TTF) $_4$ (H $_3$ O)Ru(C $_2$ O $_4$ ) $_3$ ·G where G = PhBr, PhCl, or PhF.

### 3. Materials and Methods

Bromobenzene, chlorobenzene, fluorobenzene, ethanol, and 18-crown-6 were purchased from Sigma Aldrich and used as received. BEDT-TTF was purchased from Sigma Aldrich (Gillingham, Dorset, UK) and recrystallised from chloroform.

#### 3.1. Synthesis

Ammonium tris(oxalato)aluminate and tri(oxalato)cobaltate were synthesised by the method of Bailar and Jones [59]. Ammonium tris(oxalato)ruthenate was synthesised by the method of Kaziro et al [60].

**Al-PhBr:** One-hundred milligrams of ammonium tris(oxalato)aluminate and 200 mg of 18-crown-6 ether were dissolved in 10 mL 1,2,4-trichlorobenzene, 10 mL bromobenzene, and 2 mL ethanol. The solution was then filtered into the cathodic side of the H-cell, while 20 mg of BEDT-TTF was added to the anodic side of the H-cell. The level of solvent was allowed to equilibrate in the cell, and a platinum electrode was added to each side. A constant current of 0.8  $\mu$ A was applied across the H-cell which gave small black crystals of **Al-PhBr** which were collected after 28 days.

**Co-PhBr:** One-hundred milligrams of ammonium tris(oxalato)cobaltate and 200 mg of 18-crown-6 ether were dissolved in 10 mL 1,2,4-trichlorobenzene, 10 mL bromobenzene, and 2 mL ethanol. Ten milligrams of BEDT-TTF were added to the anodic side of the H-cell. A constant current of 0.6  $\mu$ A was applied across the H-cell which gave tiny black crystals of **Co-PhBr** which were collected after 14 days.

**Ru-PhF:** One-hundred milligrams of ammonium tris(oxalato)ruthenate and 200 mg of 18-crown-6 ether were dissolved in 10 mL 1,2,4-trichlorobenzene, 10 mL fluorobenzene, and 2 mL ethanol. Ten milligrams of BEDT-TTF were added to the anodic side of the H-cell. A constant current of 1.0  $\mu$ A was applied across the H-cell which gave black block crystals of **Ru-PhF** which were collected after 28 days.

**Ru-PhCl:** One-hundred milligrams of ammonium tris(oxalato)ruthenate and 200 mg of 18-crown-6 ether were dissolved in 10 mL 1,2,4-trichlorobenzene, 10 mL chlorobenzene, and 2 mL ethanol. Ten milligrams of BEDT-TTF were added to the anodic side of the H-cell. A constant current of 1.0  $\mu$ A was applied across the H-cell which gave black block crystals of **Ru-PhCl** which were collected after 28 days.

**Ru-PhBr:** One-hundred milligrams of ammonium tris(oxalato)ruthenate and 200 mg of 18-crown-6 ether were dissolved in 10 mL 1,2,4-trichlorobenzene, 10 mL chlorobenzene, and 2 mL ethanol. Ten milligrams of BEDT-TTF were added to the anodic side of the H-cell.



A constant current of 1.0  $\mu\text{A}$  was applied across the H-cell which gave thin needle crystals of **Ru-PhBr** which were collected after 28 days. The crystals were very thin and not suitable for a publishable X-ray dataset.

### 3.2. Single-Crystal X-ray Crystallography

Data were collected using a RigakuRapid II (Tokyo, Japan) imaging plate system with the MicroMax-007 HF/VariMax rotating-anode X-ray generator and confocal monochromated Mo-K $\alpha$  radiation.

### 3.3. Conducting Properties

Out-of-plane electrical resistance was measured using the standard four-terminal AC method with the current along the  $c^*$  axis. Four gold wires were attached using carbon paint on both plane surfaces of single crystals.

## 4. Conclusions

We reported the synthesis and characterization of  $\beta''$ -(BEDT-TTF) $_4$ (H $_3$ O)Al(C $_2$ O $_4$ ) $_3$ ·C $_6$ H $_5$ Br (**Al-PhBr**), which represents the first superconductor in the Day series to contain the tris(oxalato)aluminate anion. This salt ( $M = \text{Al}$ ) is isostructural with bromobenzene salts where  $M = \text{Fe, Ga, Rh, Ru, Mn, Cr}$ . A relationship between the  $b$  axis length and superconducting  $T_c$  has previously been observed in the Day series [31]. The  $b$  axis length of these bromobenzene salts at room temperature showed that the  $M = \text{Fe}$  salt had the longest  $b$  axis and also the highest  $T_c$  of  $\sim 3.8$  K, while  $M = \text{Al}$  had the shortest  $b$  axis and the lowest  $T_c$  of  $\sim 2.5$  K. We also reported the isostructural  $M = \text{Co}$  salt (**Co-PhBr**), which did not show superconductivity. The  $b$  axis of this salt was much shorter than all other bromobenzene salts. Isostructural salts **Ru-PhCl** and **Ru-PhF** were presented in which the  $b$  axes were longer than that observed in superconducting **Al-PhBr**, but these two ruthenium salts did not show superconductivity. This indicates that even though the  $b$  axis length predominantly affected the electronic state, including the  $T_c$ , other factors may also be at work, such as the shape and the electric dipole of the guest molecules, which may have minor influences on the electronic states.

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