

# Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Charge transfer salts of BEDT-TTF with lithium tris(oxalato)metallate(III)

Lee Martin,<sup>a\*</sup> Hendrik Engelkamp,<sup>a</sup> Hiroki Akutsu,<sup>b,c</sup> Shin'ichi Nakatsuji,<sup>c</sup> Jun'ichi Yamada,<sup>c</sup> Peter Horton<sup>d</sup> and Michael B. Hursthouse<sup>d</sup>

<sup>5</sup> Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

**The first radical cation salts in the extensive family (BEDT-TTF)<sub>x</sub>[(A)M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]. Guest containing lithium as the counter cation have been synthesized and characterised.**

Crystal engineering of bis(ethylenedithio)tetrathiafulvane (BEDT-TTF) radical cation salts has been investigated extensively to combine various physical properties in the segregated anionic and cationic layers. The largest known family of these salts is that of BEDT-TTF with tris(oxalato)metallate anions which combine magnetism with a variety of electronic ground states. This family of salts has the general formula (BEDT-TTF)<sub>x</sub>[(A)M<sup>3+</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]. Guest (A = K<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>; M<sup>3+</sup> = Fe,<sup>1</sup> Cr,<sup>2</sup> Ga,<sup>3</sup> Al,<sup>4</sup> Co,<sup>4</sup> Ru<sup>5</sup>, Cu<sup>6</sup>) which crystallise in a number of different polymorphs. The packing arrangement of the donor layers, and therefore conducting behaviour of these salts, is influenced by the packing arrangement of the anionic layers. The tris(oxalato)metallate anions form a hexagonal network with the counter cation (A) producing a honeycomb of cavities which are able to include a guest molecule of the electrolyte which is being used for the electrochemical synthesis. Changes to the size and shape of this guest electrolyte molecule leads to changes in the hydrogen bonding interactions between the insulating anionic layer and the conducting cationic layer. Subtle changes to packing of this cationic layer produces a range of electronic ground states.<sup>7</sup> β'' donor packing is observed in the majority of these salts and has shown superconductivity in many cases (M = Fe<sup>3+</sup>, Guest = PhCN, PhNO<sub>2</sub>, PhBr, PhF), metallic (M = Fe<sup>3+</sup>, Guest = PhCl, DMF), semiconducting (M = Fe<sup>3+</sup>, Guest = PhI) or metal-insulator behaviour (M = Fe<sup>3+</sup>, Guest = dichloromethane or pyridine).<sup>7</sup>

In some cases the electrolyte molecule is too large to be included in the hexagonal cavity *e.g.* 1,2,4-trichlorobenzene,<sup>8</sup> carvone.<sup>9</sup> However it has been shown that 1,2,4-trichlorobenzene is an excellent solvent in which to grow crystals of this type in combination with a smaller guest molecule plus ethanol.<sup>8</sup>

Different polymorphs have been observed when the guest electrolyte molecule is only slightly too large to fit within the cavity. These molecules are arranged asymmetrically within the cavity and some part of the molecule will protrude from the anionic layer into the cationic layer. This results in the two faces of the anionic layer presenting a different face to each adjacent cationic layer which leads to alternate cationic layers having different donor packing motifs and different electronic

ground states. α-Pseudo-κ packing has been observed with metallic behaviour (Guest = 1,2-dibromobenzene)<sup>10</sup> whilst a metal-insulator transition is observed in the α-β'' phases (Guest = PhN(CH<sub>3</sub>)COH, PhCH<sub>2</sub>CN or PhCOCH<sub>3</sub>).<sup>11</sup> Another α-β'' phase is found with *sec*-phenethyl alcohol as guest molecule showing small differences in the metal-insulator behaviour depending on whether racemic or a single enantiomer of the electrolyte is used.<sup>11</sup>

The distribution of the enantiomers of tris(oxalato)metallate can also lead to different polymorphs with different electronic properties. In the β'' salts each anion layer consists of only a single enantiomer, with neighbouring layers consisting of only the opposite enantiomer. When synthesising these crystals from enantiopure M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> racemisation occurs during growth and leads to a semiconducting polymorph with a pseudo-κ donor packing motif and anionic layers which contains a 50:50 mixture of Δ- and Λ-M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> in alternate rows.<sup>12</sup>

Research on these salts has focussed on the use of K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> as the counter cations. We recently reported the inclusion of Na<sup>+</sup> in the first chiral examples of this family synthesised using electrocrystallisation from chiral electrolyte (*R*)-carvone and racemic Na<sub>3</sub>Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> to give semiconducting (BEDT-TTF)<sub>3</sub>NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>. Guest containing a single enantiomer of Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.<sup>9</sup>

In this work we report the synthesis and characterisation of a new polymorph in the first BEDT-TTF salts in this family by introducing lithium as the counter cation.

## Experimental

### Synthesis and purification of starting materials

Li<sub>3</sub>Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and Li<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> were synthesised by an adaptation of the method of Bailar and Jones.<sup>13</sup> BEDT-TTF, acetonitrile, dichloromethane, ethanol, L-carvone and 12-crown-4 (Aldrich) were used as received.

Electrocrystallisations were carried out in conventional H-shaped cells with a volume of 40mL containing 10mg BEDT-TTF in the anode compartment. H-cells were placed in sand-filled compartments in the dark at constant temperature of 293K. The H-cells had two platinum electrodes, separated by a porous glass frit to prevent contamination. The electrodes were cleaned by applying a voltage across the electrodes in 1 M H<sub>2</sub>SO<sub>4</sub> in each direction resulting in the evolution of H<sub>2</sub> and O<sub>2</sub> at the electrodes. Finally the electrodes were washed in distilled water and thoroughly dried.

**Synthesis of (BEDT-TTF)<sub>4</sub>(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> (I)**

120mg Li<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and 15mg 12-crown-4 crown ether were mixed for six hours in 10mL acetonitrile and 10mL dichloromethane. The solution was transferred to the H-cell and a layer of 2mL water was added to the anode side of the H-cell. A constant current of 1.0μA was passed through the solution in a H-shaped cell and black spear-shaped crystals grew on the anode and were collected after 6 days.

**Synthesis of (BEDT-TTF)<sub>3</sub>LiCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.ethanol (II)**

134mg Li<sub>3</sub>Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and 5 drops of 12-crown-4 crown ether were mixed in 20mL L-carvone and 20mL ethanol for three hours. A constant current of 0.1 μA was passed through the solution in a H-shaped cell and black crystals grew on the anode and were collected after 1 month.

**Synthesis of (BEDT-TTF)<sub>3</sub>LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.ethanol (III)**

106mg Li<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and 5 drops of 12-crown-4 crown ether were mixed in 20mL L-carvone and 20mL ethanol for three hours. A constant current of 0.1μA was passed through the solution in a H-shaped cell and black crystals grew on the anode and were collected after 1 month.

**Physical measurements**

Two-probe DC transport measurements were made on several crystals of both **I-III** using a HUSO HECS 994C multi-channel conductometer. Gold wires (15 μm diameter) were attached to the crystal, and the attached wires were connected to a four-pin integrated circuit plug with gold conductive cement.

**Discussion**

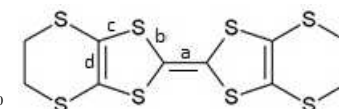
Radical cation salts **I-III** all consist of alternating layers of tris(oxalato)metallate and BEDT-TTF. The anionic layers for **I** contain a novel honeycomb network of Li<sup>+</sup> and M(oxalate)<sub>3</sub><sup>3-</sup> with includes a water molecule which elongates the hexagon in one direction (Li...Fe distances of 5.33(1), 5.31(1) and 8.00(1) Å). The anionic layers for **II** and **III** contain a honeycomb network of Li<sup>+</sup> and M(oxalate)<sub>3</sub><sup>3-</sup> with a guest molecule situated in the hexagonal cavity. The Li...M distances are shorter than the O...M or K...M distances found in the β'' superconducting phases where H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup> or K<sup>+</sup> is the counter cation. The resulting hexagonal cavities are therefore smaller in size in these lithium salts and smaller guest molecules are possible in these salts. This is similar to the sodium salts previously reported with nitromethane and dichloromethane,<sup>9</sup> as opposed to the β'' phases where larger guests such as benzonitrile, nitrobenzene or chlorobenzene are included.<sup>1-5</sup>

**η-(BEDT-TTF)<sub>4</sub>(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> (I)** crystallises in monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c* (Fig. 1). The asymmetric unit of **I** consists of four crystallographically independent BEDT-TTFs which adopt an η packing motif (Fig. 2). Within each of the donor stacks there are no close S...S contacts below the van der Waals distance. There are a large number side-to-side contacts between donor stack with the shortest contact of S7...S11 3.29(1) Å. From the donor C=C and C-S bond lengths<sup>14</sup> (Table 1) it can be approximated that the four

crystallographically independent BEDT-TTF molecules have charges of 0.74<sup>+</sup>, 0.39<sup>+</sup>, 0.43<sup>+</sup> and 0.39<sup>+</sup>. An overall charge on (BEDT-TTF)<sub>4</sub> of 1.95<sup>+</sup> ± 0.4 is constant with the formula with [(H<sub>2</sub>O)LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup>.

Each anionic layer in **I** consists of alternating segregated rows of either Δ- or Λ-Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> to give an overall racemic lattice. Unlike any salt found previously in this family the honeycomb network created by the Fe<sup>3+</sup> and Li<sup>+</sup> is elongated along the *c* axis by the inclusion of a H<sub>2</sub>O molecule in the same cavity where Li<sup>+</sup> is located (Fig. 3). On the other hand, the large hexagonal cavity is empty as shown in Fig. 3 although the cavity is occupied by an incorporated solvent molecule in the previously obtained oxalate salts. A PLATON SQUEEZE analysis suggests that the void size is 165 Å<sup>3</sup> where approximately 60 electrons exists (see supplementary cif file). We used two solvents, CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>, the electron numbers of which are 21 and 48, respectively. So we guess that the void is occupied by CH<sub>2</sub>Cl<sub>2</sub> that is heavily disordered. It was not possible to resolve the highly disordered solvent molecules within the hexagonal cavities. This makes the *R*-value relatively high. Two-probe resistivity measurements were made on a single crystal and show that **I** is a semiconductor with an activation energy of 0.080eV and a room temperature resistivity of ρ<sub>RT</sub> of 2.41 Ohm.cm.

**Table 1** Average bond lengths in BEDT-TTF molecules of **I-III** and approximation of charge on the molecules. δ = (b+c)-(a+d), Q = 6.347-7.463δ.<sup>14</sup>



Salt	Donor	a / Å	b / Å	c / Å	d / Å	δ	Q	Total charge
<b>I</b>	A	1.375	1.730	1.748	1.349	0.752	0.74+	
	B	1.355	1.738	1.753	1.329	0.798	0.39+	
	C	1.351	1.743	1.745	1.345	0.793	0.43+	
	D	1.356	1.747	1.748	1.378	0.772	0.39+	1.95 ± 0.4
<b>II</b>	A x2	1.389	1.721	1.744	1.360	0.716	1.00+	
	B	1.310	1.760	1.745	1.346	0.849	0.01+	2.01 ± 0.2
<b>III</b>	A x2	1.420	1.736	1.767	1.336	0.747	0.77+	
	B	1.319	1.783	1.756	1.324	0.896	0.34+	1.94 ± 0.2

**(BEDT-TTF)<sub>3</sub>LiCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.ethanol (II)** and **(BEDT-TTF)<sub>3</sub>LiFe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.ethanol (III)** (Fig. 4-6) are isostructural and both crystallise in monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c*. They are isostructural with (BEDT-TTF)<sub>3</sub>NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub><sup>9</sup> reported previously which crystallises in the space group *P*<sub>2</sub><sub>1</sub>. Both the sodium and lithium analogues were synthesised from carvone as the electrolyte which has been shown to produce chiral materials in this family. The sodium analog is a racemic twin containing only a single enantiomer of D-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>, whilst in **II** and **III** there is 50:50 disorder of the M<sup>3+</sup>:Li sites

giving an overall racemic lattice. The ethanol guest molecule is situated in the hexagonal cavity disordered over two sites with OH groups protruding out on both sides of the anion layer (Fig. 4).

The same donor packing motif is observed for both **II** and **III**, which are isostructural with (BEDT-TTF)<sub>3</sub>NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub>.<sup>9</sup> Pairs of donor molecules (A) are parallel to one another (B) with a third molecule twisted at 45° with respect to the other pair (Fig. 5). There are no face-to-face close S...S contacts between the BEDT-TTF A donors but there are four side-to-side close contacts between the two crystallographically independent donor molecules, A and B (Table 2). These S...S contacts are all shorter in the chromium salt **II** compared to the iron salt **III**.

**Table 2** S...S contacts shorter than the van der Waals distance for **II** and **III**.

	<b>II</b>	<b>III</b>
S1...S10	3.43(1)	3.49(1)
S1...S12	3.47(1)	3.52(1)
S5...S9	3.57(1)	3.64(1)
S7...S9	3.49(1)	3.57(1)

Table 1 shows the C=C and C-S bond lengths for both **II** and **III**. For each [LiM(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> unit there are three BEDT-TTF molecules, two of which have a charge close to 1<sup>+</sup> with the other one having a charge close to 0. Therefore the A donor is a cation and forms a diamagnetic spin dimer, whilst the B donor is neutral and surrounded by the A dimers. Such a charge disproportionation gives poor conductivity. These donor charges shows a significant difference compared to the isostructural sodium salt (BEDT-TTF)<sub>3</sub>NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub> where charges on each of the three donor molecules are calculated as 0.77<sup>+</sup>, 0.75<sup>+</sup>, and 0.55<sup>+</sup>, giving a total of 2.07<sup>+</sup> ± 0.3.

Two-probe resistivity measurements were made on a single crystal and show that both **II** and **III** are semiconductors. Salt **II** has an activation energy of 0.129 eV and a room temperature resistivity of  $\rho_{RT}$  of 197 Ohm.cm, whilst **III** has an activation energy of 0.126 eV and  $\rho_{RT}$  of 98.1 Ohm.cm. By comparison the isostructural sodium salt (BEDT-TTF)<sub>3</sub>NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub> has an activation energy of 0.079 eV and  $\rho_{RT}$  of 22 Ohm.cm.

## Conclusions

We have synthesized the first examples of radical cation salts of BEDT-TTF with tris(oxalato)metallates having lithium as the counter cation. In salt **I** a novel anion layer packing arrangement is observed with a hexagonal cavity which is elongated in one direction and leads to a donor packing motif not previously observed in this family of salts. Salts **II** and **III** have smaller hexagonal cavities than observed in previous salts of this family and have a preference for smaller solvents such as ethanol. Salts **II** and **III** have been synthesized using L-carvone as electrolyte which has previously led to chiral [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> layers in the isostructural sodium salt, (BEDT-TTF)<sub>3</sub>NaCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·CH<sub>3</sub>NO<sub>2</sub>. However, the lithium salts

reported here exist as a 50:50 racemic mixture owing to the disorder of the Li<sup>+</sup> and M<sup>3+</sup> sites within the anionic layers. Future work will investigate the inclusion of other electrolytes into salts of LiM(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> with BEDT-TTF to see if chirality can be observed.

LM thanks the Royal Society of Chemistry for a Journals Grant for International Authors. This work has been supported by the Royal Society [Research Grants (RG100853 and RG081209), International Exchange Scheme (IE130367), and International Joint Project (JP0869972)]. We thank EPSRC for funding the National Crystallography Service.

## Notes and references

<sup>a</sup> School of Science and Technology, Nottingham Trent University, Clifton Lane, Clifton, Nottingham, NG11 8NS, UK. Fax: +44 (0)1158483128; Tel: +44 (0)1158483128; E-mail: lee.martin@ntu.ac.uk

<sup>b</sup> Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan

<sup>c</sup> Graduate School of Material Science, University of Hyogo, Kamigori-cho, Ako-gun, Hyogo, 678-1297, Japan.

<sup>d</sup> School of Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, Highfield, Southampton, SO17 1BJ, UK

<sup>†</sup> Crystal data: **I**: C<sub>46</sub>H<sub>34</sub>FeLiO<sub>13</sub>S<sub>32</sub>, *M* = 1883.44, dark brown blade, *a* = 8.7086(5), *b* = 37.248(2), *c* = 22.1051(14) Å,  $\alpha$  = 90°,  $\beta$  = 90.193(3)°,  $\gamma$  = 90°, *U* = 7170.4(8) Å<sup>3</sup>, *T* = 120(2) K, space group *P2<sub>1</sub>/n*, *Z* = 4,  $\mu$  = 1.199 mm<sup>-1</sup>, reflections collected = 64973, independent reflections = 16261, *R*1 = 0.1023, *wR*2 = 0.1930 [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)], *R*1 = 0.1341, *wR*2 = 0.2080 (all data).

All hydrogen atoms were fixed using a standard riding model.

There was some highly disordered solvent within the oxalate cavities which could not be resolved and thus removed from the calculations using the SQUEEZE program.

Crystal data: **II**: C<sub>38</sub>H<sub>30</sub>CrLiO<sub>13</sub>S<sub>24</sub>, *M* = 1891.68, black plate, *a* = 18.198(6), *b* = 14.951(4), *c* = 10.109(3) Å,  $\alpha$  = 90°,  $\beta$  = 93.127(6)°,  $\gamma$  = 90°, *U* = 2746.2(14) Å<sup>3</sup>, *T* = 296(2) K, space group *P2<sub>1</sub>/c*, *Z* = 2,  $\mu$  = 14.977 cm<sup>-1</sup>, reflections collected = 12600, independent reflections = 4754, *R*1 = 0.0975 [*I* > 2σ], *R*1 = 0.1512, *wR*2 = 0.2349 (all data).

Crystal data: **III**: C<sub>38</sub>H<sub>30</sub>FeLiO<sub>12</sub>S<sub>24</sub>, *M* = 1891.68, black plate, *a* = 18.491(11), *b* = 15.146(9), *c* = 10.292(6) Å,  $\alpha$  = 90°,  $\beta$  = 93.363(16)°,  $\gamma$  = 90°, *U* = 2873(3) Å<sup>3</sup>, *T* = 302(2) K, space group *P2<sub>1</sub>/c*, *Z* = 2,  $\mu$  = 11.905 cm<sup>-1</sup>, reflections collected = 21364, independent reflections = 6489, *R*1 = 0.1309 [*I* > 2σ], *R*1 = 0.2330, *wR*2 = 0.3672 (all data).

Crystals of **I** were run on Bruker-Nonius KappaCCD diffractometer with Mo rotating anode, using standard control and processing software. All structures were solved and refined with programs from the SHELX family

Crystals of **II** and **III** were run using a Rigaku Mercury II CCD configured with the Rigaku MicroMax-007HF generator and VariMax confocal mirror, at room temperature. Control of the machine and the data processing were performed by the Rigaku CrystalClear ® software package. The structures were solved using SIR92 for **II** and SIR 2008 for **III** and refined by SHELX2010 and the Rigaku CrystalStructure ® software package.

CCDC 1042692, 1042693 and 1042696 contains supplementary X-ray crystallographic data for **I**, **II** and **III**. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax: (+44) 1223-336-033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

- 1 M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse and P. Guionneau, *J. Am. Chem. Soc.*, 1995, **117**, 12209; E. Coronado, S. Curreli, C. Giménez-Saiz and C. J. Gómez-García, *J. Mater. Chem.*, 2005, **15**, 1429.
- 2 L. Martin, S. S. Turner, P. Day, F. E. Mabbs and E. J. L. McInnes, *J. Chem. Soc., Chem. Commun.*, 1997, 1367; S. Rashid, S. S. Turner, P. Day, J. A. K. Howard, P. Guionneau, E. J. L. McInnes, F. E. Mabbs, R. J. H. Clark, S. Firth and T. Biggs, *J. Mater. Chem.*, 2001, **11**, 2095.
- 3 H. Akutsu, A. Akutsu-Sato, S. S. Turner, D. Le Pevelen, P. Day, V. Laukhin, A.-K. Klehe, J. Singleton, D. A. Tocher, M. R. Probert, and J. A. K. Howard, *J. Am. Chem. Soc.*, **2002**, *124* (42), 12430; T. Prokhorova, L. I. Buravov, E. B. Yagubskii, L. V. Zorina, S. V. Simonov, R. P. Shibaeva and V. N. Zverev, *Eur. J. Inorg. Chem.*, 2014, **24**, 3933.
- 4 L. Martin, S. S. Turner, P. Day, P. Guionneau, J. K. Howard, D. E. Hibbs, M. E. Light, M. B. Hursthouse, M. Uruichi and K. Yakushi, *Inorg. Chem.*, 2001, **40**, 1363.
- 5 T. G. Prokhorova, L. V. Zorina, S. V. Simonov, V. N. Zverev, E. Canadell, R. P. Shibaeva and E. B. Yagubskii, *CrystEngComm*, 2013, **15**, 7048.
- 6 B. Zhang, Y. Zhang and D. Zhu, *Chem. Commun.*, 2012, **48**, 197.
- 7 S. S. Turner, P. Day, D. E. Hibbs, K. M. A. Malik, M. B. Hursthouse, S. J. Teat, E. J. MacLean, L. Martin and S. A. French, *Inorg. Chem.*, 1999, **38**, 3543; S. Rashid, S. S. Turner, D. Le Pevelen, P. Day, M. E. Light, M. B. Hursthouse, S. Firth and R. J. H. Clark, *Inorg. Chem.*, 2001, **40**, 5304; T. G. Prokhorova, S. S. Khasanov, L. V. Zorina, L. I. Buravov, V. A. Tkacheva, A. A. Baskakov, R. B. Morgunov, M. Gener, E. Canadell, R. P. Shibaeva and E. B. Yagubskii, *Adv. Funct. Mater.*, 2003, **13**, 403; E. Coronado, S. Curreli, C. Giménez-Saiz and C. J. Gómez-García, *J. Mater. Chem.*, 2005, **14**, 1429.
- 8 T. G. Prokhorova, L. I. Buravov, E. B. Yagubskii, L. V. Zorina, S. S. Khasanov, S. V. Simonov, R. P. Shibaeva, A. V. Korobenko and V. N. Zverev, *CrystEngComm* 2011, **13**, 537.
- 9 L. Martin, P. Day, P. Horton, S. Nakatsuji, J. Yamada and H. Akutsu, *J. Mater. Chem.*, 2010, **20**, 2738; L. Martin, P. Day, S. Nakatsuji, J. Yamada, H. Akutsu and P. Horton, *CrystEngComm*, 2010, **12**, 1369; L. Martin, H. Akutsu, P. Horton and M. B. Hursthouse, *CrystEngComm*, 2015, DOI: 10.1039/C5CE00121H.
- 10 L. V. Zorina, S. S. Khasanov, S. V. Simonov, R. P. Shibaeva, V. N. Zverev, E. Canadell, T. G. Prokhorova and E. B. Yagubskii, *CrystEngComm*, 2011, **13**, 2430.
- 11 H. Akutsu, A. Akutsu-Sato, S. S. Turner, P. Day, E. Canadell, S. Firth, R. J. H. Clark, J.-i. Yamada and S.-i. Nakatsuji, *Chem. Commun.*, 2004, 18; L. Martin, P. Day, H. Akutsu, J. Yamada, S. Nakatsuji, W. Clegg, R. W. Harrington, P. N. Horton, M. B. Hursthouse, P. McMillan and S. Firth, *CrystEngComm*, 2007, **9**, 865.
- 12 L. Martin, S. S. Turner, P. Day, K. M. A. Malik, S. J. Coles, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1999, 513; L. Martin, S. S. Turner and P. Day, *Synth. Met.*, 1999, **102**, 1638.
- 13 J. C. Bailar and E. M. Jones, *Inorg. Synthesis* 1939, **1**, 1993.
- 14 P. Guionneau, C. J. Kepert, D. Chasseau, M. R. Truter and P. Day, *Synth. Met.*, 1997, **86**, 1973.

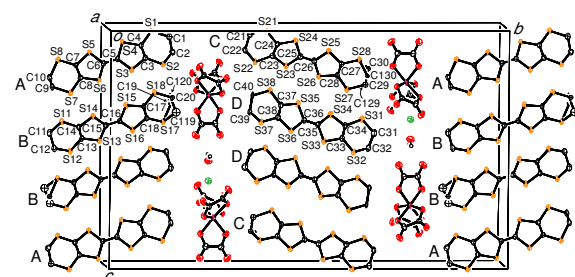


Fig. 1 Layered structure of **I** showing atomic labels of four crystallographically independent BEDT-TTF molecules, A, B, C and D. Hydrogens apart from those of water molecules are omitted for clarity.

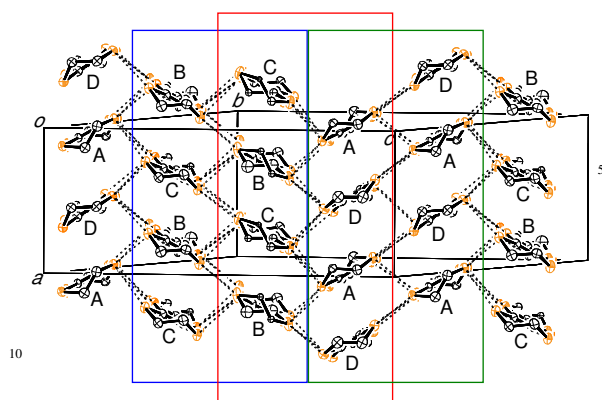


Fig. 2 BEDT-TTF layer of **I** viewed along the molecular long axis with S...S contacts below the sum of the van der Waals radii ( $<3.7 \text{ \AA}$ ). Hydrogens are omitted for clarity. The donors surrounded by blue and green squares are arranged with  $\beta''$ -type packing motifs. However, the blue donors and green donors are not parallel, the dihedral angles of which are approximately  $120^\circ$  ( $118.4$ - $121.7^\circ$ ). Therefore, the donors surrounded by a red square have an  $\alpha$ -type packing motif. The donor packing arrangement has been previously observed in  $\eta$ -(BEDT-TTF)<sub>2</sub>[Au(CN)<sub>2</sub>]<sup>F1</sup> and  $\alpha''$ -(BEDT-TTF)<sub>2</sub>KCu(SCN)<sub>4</sub>.<sup>F2</sup> We hereafter call this packing type  $\eta$ -type.

<sup>F1</sup> M. Kurmoo, P. Day, T. Mitani, H. Kitagawa, H. Shimoda, D. Yoshida, P. Guionneau, Y. Barrans, D. Chasseau, and L. Ducasse, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1233.

<sup>F2</sup> H. Mori, T. Okano, N. Sakurai, S. Tanaka, K. Kajita, and H. Moriyama, *Chem. Lett.*, 1998, 505.

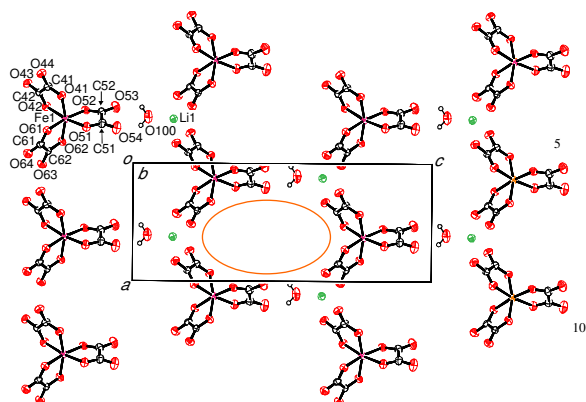


Fig. 3 Anion layer of **I** viewed down the *c* axis with atomic labels. The orange ellipsoid indicates a void (see text).

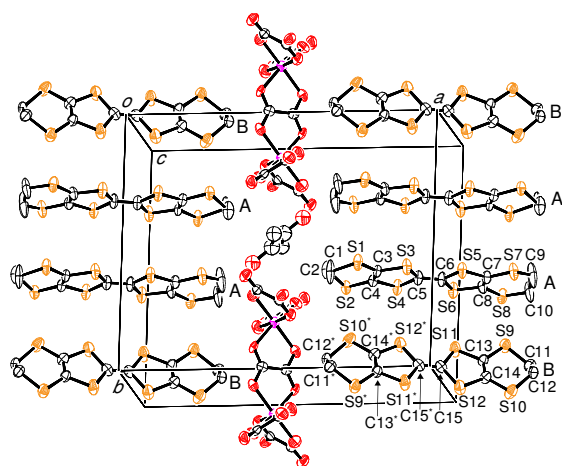


Fig. 4 Layered structure of **II** showing atomic labels of two crystallographically independent BEDT-TTF molecules, A and B. The structure of **II** is isomorphous to that of **III** and both numbering schemes are also the same. Hydrogens are omitted for clarity.

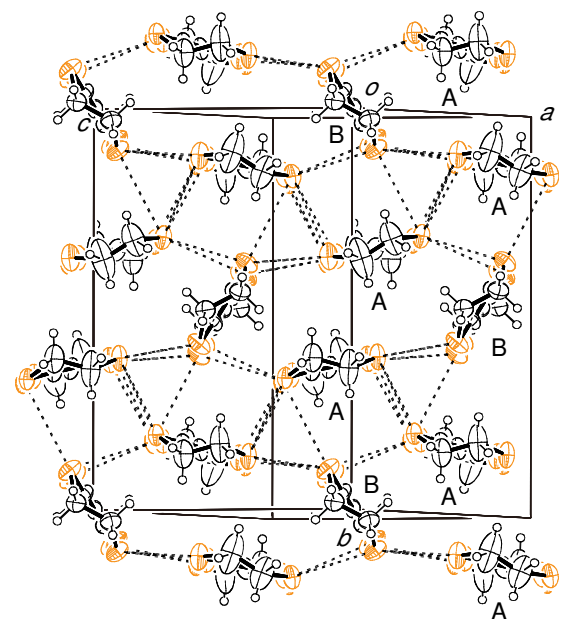


Fig. 5 BEDT-TTF layer of **II** viewed along the molecular long axis with S...S contacts below the sum of the van der Waals radii ( $<3.7$  Å). The donor arrangements of **II** and **III** are both the same.

10

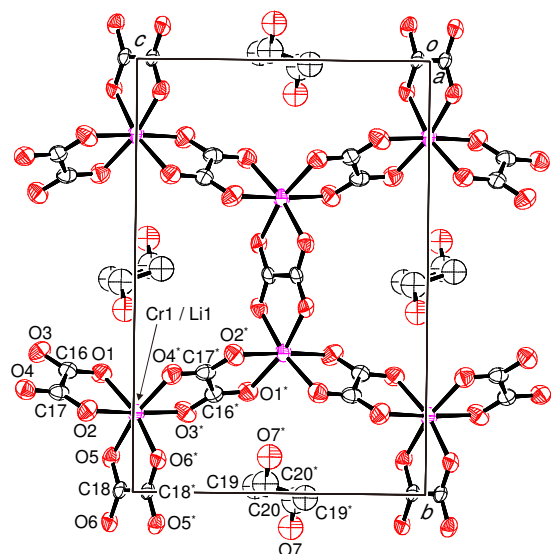
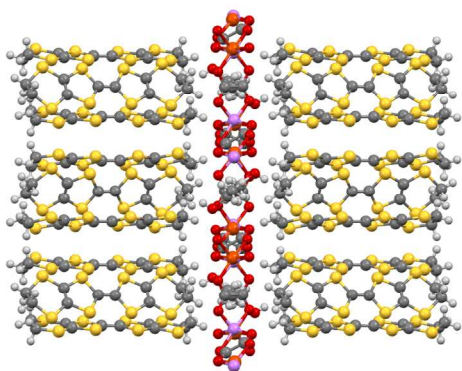


Fig. 6 Anion layer of **II** viewed down the  $c$  axis with atomic labels. Hydrogens are omitted for clarity. The atomic coordinates and the numbering schemes of **II** and **III** are both the same.



363x143mm (120 x 120 DPI)