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ARTICLE

Molecular conductors from bis(ethylenedithio)tetrathiafulvalene with tris(oxalato)rhodate

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This article reports a family of new radical-cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with tris(oxalato)rhodate: three salts with the formula β''-(BEDT-TTF)$_4$[(cation)Rh(C$_2$O$_4$)$_3$].solvent (solvent = fluorobenzene, chlorobenzene, or bromobenzene) and one with the formula pseudo κ-(BEDT-TTF)$_4$[(H$_3$O)Rh(C$_2$O$_4$)$_3$].benzonitrile. We report here the synthesis, crystal structure, electrical properties and Raman spectroscopy of these new molecular conductors. The bromobenzene salt shows a decrease in resistivity below 2.5K indicative of a superconducting transition and a Shubnikov-de Haas oscillation with a frequency of 232 T and effective mass m^* of 1.27m_e.

The synthesis of organic-inorganic hybrid materials offers the opportunity to combine two or more properties within the same crystal lattice. An extensive family of BEDT-TTF radical-cation salts with tris(oxalato)metallate anions has been discovered which combine conductivity with paramagnetism,[1] ferromagnetism[2] or anti-ferromagnetism.[3]

Within this family of formula (BEDT-TTF)$_x$[(cation)M(C$_2$O$_4$)$_3$].solvent (x = 3 or 4) the anion layer is composed of a hexagonal network of tris(oxalato)metallate with the counter cation (cation = H$_3$O$^+$, K$^+$, NH$_4^+$, Na$^+$, Li$^+$). The honeycomb cavities are occupied by a guest molecule of the electrolyte, the size and shape of which influences the arrangement of the BEDT-TTF donor layer *via* hydrogen bonding interactions. Several series of different polymorphs have been synthesized by changing the metal, counter cation, or electrolyte.

The monoclinic series with a β'' type BEDT-TTF donor packing motif is the most interesting owing to the variety of observed conducting properties from semiconductors, to metals and superconductors. These salts are synthesized from ammonium or potassium tris(oxalato)metallate(III) to produce β''-(BEDT-TTF)$_4$[(cation)Metal^{3+}(C$_2$O$_4$)$_3$].solvent (cation = K$^+$, H$_3$O$^+$, NH$_4^+$; Metal = Fe,[1,4] Cr,[4c,5] Ga,[6] Ru[7] Mn[4b]) with the highest superconducting Tc of 7.0-8.5K for β''-(BEDT-TTF)$_4$[(H$_3$O)Fe(C$_2$O$_4$)$_3$].benzonitrile.[1] A single anion layer in the β'' salts contains a single enantiomer of the tris(oxalato)metallate anion, whilst neighbouring anion layers consist entirely of the opposite enantiomer. An orthorhombic series (BEDT-TTF)$_4$[(cation)Metal^{3+}(C$_2$O$_4$)$_3$].solvent (cation = K$^+$, H$_3$O$^+$, NH$_4^+$; Metal = Fe,[1,4a,4c-e] Cr,[4c,5] Co,[4c] Al,[4c] Ru[7], Mn[8]) with a pseudo-κ BEDT-TTF packing motif has been produced in which every anion layer is identical and contains a 50:50 mixture with Δ and Λ enantiomers in alternate rows.

By using smaller guest molecules and counter cations a 3:1 series having the formula (BEDT-TTF)$_3$[(cation)Metal^{3+}(C$_2$O$_4$)$_3$].solvent (cation = Li$^+$, Na$^+$, NH$_4^+$; Metal = Fe,[9] Cr,[9-11] Al[11]) has been produced. When using larger guest molecules these sit asymmetrically in the anion layer's hexagonal cavity which leads to them protruding more on one side of the layer than the other side. This produces 4:1 multi-layered salts where adjacent donor layers each have a different packing type *e.g.* α-β'' [12] or α-κ.[13]

Changing the counter cation has also produced a variety of different phases such as (BEDT-TTF)$_4$(H$_2$O)LiFe(C$_2$O$_4$)$_3$[9] from lithium, (BEDT-TTF)$_9$Na$_{18}$[Fe(C$_2$O$_4$)$_3$]$_8$·24H$_2$O[14] from sodium, (BEDT-TTF)$_{12}$[Fe(C$_2$O$_4$)$_3$]$_2$·nH$_2$O[15] from caesium, and (BEDT-TTF)$_5$[Fe(C$_2$O$_4$)$_3$]·CH$_2$Cl$_2$·2H$_2$O[16] from tetraethylammonium. Changing the charge on the metal from 3+ to 4+ using germanium produces very different phases: (BEDT-TTF)$_2$[Ge(C$_2$O$_4$)$_3$]·benzonitrile,[17] (BEDT-TTF)$_5$[Ge(C$_2$O$_4$)$_3$]$_2$,[18] (BEDT-TTF)$_7$[Ge(C$_2$O$_4$)$_3$]$_2$(CH$_2$Cl$_2$)$_{0.87}$(H$_2$O)$_{0.09}$[18] and BEDT-TTF$_4$[Ge(C$_2$O$_4$)$_3$].0.5CH$_2$Cl$_2$.[19]

Three cases have been observed where the crown ether used to aid dissolution of the anion is included in the radical-cation salt *e.g.* α-(BEDT-TTF)$_{10}$(18-crown-6)$_6$K$_6$[Fe(C$_2$O$_4$)$_3$]$_4$(H$_2$O)$_{24}$,[14] though of particular note are the metallic proton conductor β''-(BEDT-TTF)$_4$[(NH$_4$)M(C$_2$O$_4$)$_3$]$_2$.[(NH$_4$)$_2$(18-crown-6)].5H$_2$O[20] (M = Cr or Ga) and the superconductor β''-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Rh(C$_2$O$_4$)$_3$].18-crown-6.[21]

We report here the synthesis, crystal structure, electrical properties and Raman spectroscopy of four new molecular conductors which combine BEDT-TTF with the tris(oxalato)rhodate anion. Three salts have the formula β''-(BEDT-TTF)$_4$[(cation)Rh(C$_2$O$_4$)$_3$].solvent (solvent = fluorobenzene, chlorobenzene, or bromobenzene). The bromobenzene salt has a superconducting Tc of ~2.5K. The fourth salt is a semiconductor with a formula of pseudo κ-(BEDT-TTF)$_4$[(NH$_4$)Rh(C$_2$O$_4$)$_3$].benzonitrile. Along with our

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recently reported multi-layered superconductor β”-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Rh(C$_2$O$_4$)$_3$].18-crown-6 these salts represent the first examples in the large series of tris(oxalato)-BEDT-TTF salts to contain the anion tris(oxalato)rhodate.

Results and discussion

We recently reported the synthesis, crystal structure, electrical and magnetic properties of a new 2:1 superconducting phase β”-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Rh(C$_2$O$_4$)$_3$].18-crown-6.[21] This salt is the first in the large family of tris(oxalato)metallate-BEDT-TTF salts to have a superstructure and also show ambient pressure superconductivity. The superstructure arises from a guest molecule of 18-crown-6 protruding into the tris(oxalate)metallate hexagonal cavity in the anion layer. We have also synthesized a series of new 4:1 salts from the tris(oxalato)rhodate anion (Table 1).

Structure of salts I-III

β”-(BEDT-TTF)$_4$[(cation)Rh(C$_2$O$_4$)$_3$].solvent (**I-III**) crystallise in the monoclinic space group *C2/c*, with two crystallographically independent BEDT-TTF molecules, half an Rh(C$_2$O$_4$)$_3^{3-}$ anion, half a solvent molecule, and half an H$_3$O$^+$ cation for **I** and **II**, or half an NH$_4^+$ cation for **III**. The guest solvent molecules are fluorobenzene for **I**, chlorobenzene for **II**, or bromobenzene for **III**. The crystal structure is built up of alternating layers of β”-BEDT-TTF and layers of Rh(C$_2$O$_4$)$_3^{3-}$ (Fig. 1).

The anion layer in **I-III** (Fig. 2) contains Rh(C$_2$O$_4$)$_3^{3-}$ and H$_3$O$^+$ (**I** and **II**)/NH$_4^+$ (**III**) which adopt a honeycomb packing arrangement with the solvent molecule occupying the hexagonal cavity. Each anion layer contains only a single enantiomer of Rh(C$_2$O$_4$)$_3^{3-}$ with the adjacent anion layers containing only the opposite enantiomer to give an overall racemic lattice.

Table 2 details the dimensions of the hexagonal cavity and the orientation of the solvent molecule. The dimensions of the hexagonal cavity are defined by the distances *a* and *b*. δ is the angle of the benzene ring plane relative to the plane of the hexagonal cavity. Upon increasing the size of the solvent molecule from fluorobenzene (**I**) to bromobenzene (**III**) the height (h) of the cavity increases, whilst the width (w) decreases.

The size, shape and orientation of the guest solvent molecule in the hexagonal cavity is known to influence the order/disorder of the terminal ethylene groups on neighbouring BEDT-TTF molecules and thus affect the transport properties or destabilise the superconducting transition. The BEDT-TTF molecules in the salt with the solvent molecule bromobenzene have no disordered ethylene groups, whilst disorder is observed in the smaller chlorobenzene (**II**) and fluorobenzene (**I**) salts.

The asymmetric units of **I-III** contain two crystallographically independent BEDT-TTF molecules which pack in a β”-packing motif (Fig. 2). There are a number of short S…S contacts below the sum of the van der Waals radii (<3.6 Å) which are all side-to side between BEDT-TTF molecules (Table 3).

From the donor C=C and C-S bond lengths[22] (Table 4) the BEDT-TTF molecules have estimated charges of BEDT-TTF$^{0.5+}$ as expected for the formula β”-(BEDT-TTF$^{0.5+)}$)$_4$[(cation^{1+})Rh(C$_2$O$_4$)$_3$$^{3-}$].solvent. Raman spectroscopy can also estimate the charges of BEDT-TTF molecules by observing the symmetric C=C stretching frequencies which have equal contributions from the stretching vibrations of the central C=C bond and the C=C bond which connects the five- and six-membered rings.[23] Raman spectra for each of the salts **I-III** contain a strong peak at 1467 cm^{-1} and a weaker peak at 1497 (**I**), 1495 (**II**) or 1496 cm^{-1} (**III**) which is close to that expected for 0.5$^+$ and consistent with those peaks observed for other isostructural β” salts in this series.

Structure of salt IV

Pseudo κ-(BEDT-TTF)$_4$[(NH$_4$)Rh(C$_2$O$_4$)$_3$].benzonitrile (**IV**) crystallises in the orthorhombic space group *Pbcn*, with two crystallographically independent BEDT-TTF molecules, half an Rh(C$_2$O$_4$)$_3^{3-}$ anion, half a benzonitrile molecule and half of an NH$_4^+$ cation. This salt is isostructural to previously reported salts with trisoxalates of Fe,[1,4a,4c-e] Cr,[4c,5] Co,[4c] Al,[4c] Ru,[7] Mn[8]. The crystal structure is built up of alternating layers of BEDT-TTF and layers of Rh(C$_2$O$_4$)$_3^{3-}$ (Fig. 3).

The anion layer in **IV** (Fig. 4) contains Rh(C$_2$O$_4$)$_3^{3-}$ and H$_3$O$^+$ in a honeycomb packing arrangement with a benzonitrile molecule occupying the hexagonal cavity. Each anion layer contains a 50:50 mixture of Δ and Λ enantiomers of Rh(C$_2$O$_4$)$_3^{3-}$ which form rows of each enantiomer. The benzonitrile molecule is disordered over two positions with the –C≡N group directed towards the NH$_4^+$ anions (N…N 3.064(13) Å). The Rh…N(NH$_4^+$) distances show a distortion of the hexagon compared to that observed for the β” salts (**I-III**) with an increased hexagon width (Table 3) to accommodate the disordered positions of the –C≡N group.

The asymmetric unit of **IV** contains two crystallographically independent BEDT-TTF molecules which pack in a pseudo-κ packing motif with BEDT-TTF dimers each surrounded by six neutral BEDT-TTF monomers (Fig. 4). There are a number of short S…S contacts below the sum of the van der Waals radii (<3.6 Å) (Table 3). From the donor C=C and C-S bond lengths[22] (Table 4) the BEDT-TTF molecules have estimated charges of BEDT-TTF^0 and BEDT-TTF^{1+}. The Raman spectrum for salt **IV** contains peaks at 1411, 1449, 1490 and 1552 cm^{-1}. This is consistent with the peaks observed for other isostructural pseudo κ salts in this series which are composed of BEDT-TTF^{1+} and BEDT-TTF^0.

The use of benzonitrile as electrolyte with tris(oxalato)metallates of Fe,[1,4a,4c-e] or Cr,[4c,5] gives crystals of both β” and pseudo-κ polymorphs, whereas only the pseudo-κ form has been observed when the metal is Co,[4c] Al,[4c] Ru[7], Mn[8] or Rh.

Electrical properties

SQUID magnetometry was performed on bulk samples of salts **I** and **II** down to 1.8K but no superconducting transitions were observed. Electrical resistivity measurements performed on **III** using the four probe method shows low room temperature resistivity which decreases upon cooling as expected for a metal. A decrease in resistivity is observed below 2.5K indicative of a superconducting transition (Fig. 5 and 6). A Shubnikov-de Haas oscillation with a frequency of 232 T and effective mass m^* of 1.27m_e is observed.

Salt **IV** is a semiconductor, similar to isostructural salts of the phase pseudo-κ-(BEDT-TTF)$_4$[(A)M(C$_2$O$_4$)$_3$].Guest[4-7] having dimers consisting of two ET^{1+} molecules surrounded by six neutral ET molecules. Salt **IV** has an activation energy of 245 meV (Fig. 7). This E_a value is higher than those previously reported for isostructural pseudo-κ salts in the tris(oxalato)metallate series (140-225 meV).[4-8]

Experimental

Synthesis of salts I-IV

Salts **I-IV** were synthesized by dissolving 100 mg of ammonium tris(oxalato)rhodate and 200 mg 18-crown-6 ether in 10mls 1,2,4-

trichlorobenzene:2mls ethanol with 10mls fluorobenzene for **I**, chlorobenzene for **II**, bromobenzene for **III**, or benzonitrile for **IV**. This was placed in a two-compartment H-shaped electrochemical cell containing 10 mg ET in the anode compartment. A large quantity of black block (**I-III**) or black diamond (**IV**) crystals were obtained upon applying a current of 1.0 μA across the cell with 1mm diameter platinum electrodes for three weeks in a dark box on a vibration-free bench. BEDT-TTF, 18-crown-6, and all solvents were purchased from Sigma-Aldrich and were used as received. $(NH_4)_3Rh(C_2O_4)_3].xH_2O$ was prepared by the method of Werner[24] and recrystallized several times from water.

Physical measurements

Temperature dependent electrical resistivity measurements were performed using four contacts on single crystals of **III** along the out-of-plane direction in the range 0.8K-300K. Measurements were performed using two contacts on single crystals of **IV** in the range 77K-300K.

Magnetic susceptibility measurements were carried out to look for superconducting transitions by zero-field cooling samples to 1.8K and applying a small magnetic field.†

X-Ray single crystal diffraction measurements were performed using a Rigaku Oxford Diffraction Xcalibur System equipped with a Sapphire detector at room temperature using the Crysalis software.[25] Structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 using CRYSTALS.[26] Molecular illustrations were prepared with Mercury.[27]

Raman spectra were recorded at room temperature with a Renishaw InVia Raman microscope equipped with a 514nm laser at 0.1% laser power and a 1800 l mm^{-1} grating. The recorded spectra are the result of 30 seconds exposure from 1200 to 1650 cm^{-1}.

Conclusions

The tris(oxalato)rhodate anion has produced four new molecular conductors with the donor molecule BEDT-TTF to continue to expand Peter Day's large family of conducting and superconducting salts of BEDT-TTF with $M(C_2O_4)_3$. Using a halobenzene as the solvent for crystal growth produces salts with the formula β''-$(BEDT\text{-}TTF)_4[(cation)Rh(C_2O_4)_3]$.solvent whilst using benzonitrile produces a salt with the formula pseudo κ-$(BEDT\text{-}TTF)_4[(NH_4)Rh(C_2O_4)_3]$.benzonitrile. The bromobenzene salt has a superconducting Tc of ~2.5K and a Shubnikov-de Haas oscillation with a frequency of 232 T and effective mass m^* of $1.27m_e$. Along with our recently reported multi-layered superconductor β''-$(BEDT\text{-}TTF)_2[(H_2O)(NH_4)_2Rh(C_2O_4)_3]$.18-crown-6, these salts represent the first examples in the Day series to contain the anion tris(oxalato)rhodate.

Conflict of interest

There are no conflicts of interest to declare

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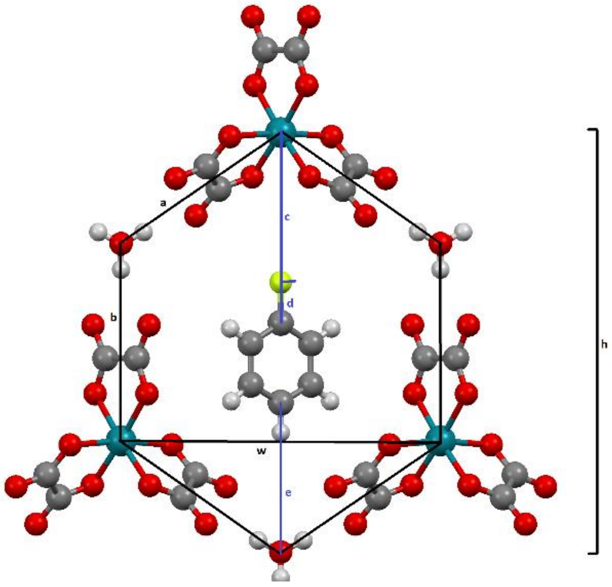
Table 1 Crystallographic data for **I-IV.**

Salt	I	II	III	IV
Formula	C52 H40 F1 O13 Rh1 S32	C52 H40 Cl1 O13 Rh1 S32	C52 H41 Br1 N1 O12 Rh1 S32	C53 H41 N2 O12 Rh1 S32
Fw [g mol^{-1}]	2020.90	2037.33	2080.82	2026.93
Crystal System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*C2/c*	*C2/c*	*C2/c*	*Pbcn*
Z	4	4	4	4
T (K)	294	295	294	292
a [Å]	10.32638(12)	10.3180(3)	10.3147(2)	10.43833(16)
b [Å]	19.9527(3)	20.0233(4)	20.0458(4)	19.6739(3)
c [Å]	35.0343(5)	35.1173(6)	35.2608(6)	35.9215(6)
α[°]	90.0	90.0	90.0	90.0
β[°]	93.1002(12)	93.5628(18)	93.7457(17)	90.0
γ[°]	90.0	90.0	90.0	90.0
Volume [Å^3]	7207.87(10)	7241.19(12)	7275.18(12)	7376.92(13)
Density [g cm^{-3}]	1.860	1.867	1.900	1.825
μ [mm^{-1}]	1.227	1.256	1.762	1.197
$R_1[I > 2\sigma(I)]$	0.0418	0.0452	0.0540	0.0580
wR [$all\ data$]	0.0821	0.0990	0.1064	0.1280



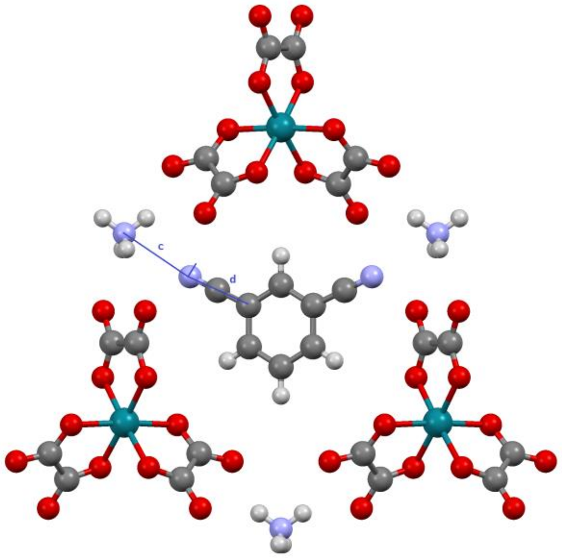


Table 2 Selected distances and angles for **I-IV**. *C2/c* scheme for **I-III** (top) and *Pbcn* scheme for **IV** (bottom).

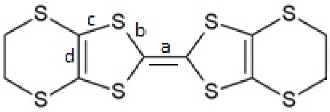
Salt	I	II	III	IV
Distances / Å				
a	6.291(3)	6.302(4)	6.312(4)	6.310(4)
b	6.382(6)	6.391(6)	6.384(6)	6.290(8)
c	4.843(14)	4.620(2)	4.6135(11)	3.064(13)
d	1.313(17)	1.732(8)	1.886(8)	2.434(14)
e	4.763(13)	4.513(12)	4.416(12)	5.442(16)
h	13.570(6)	13.632(6)	13.661(6)	13.384(8)
w	10.32638(12)	10.3180(3)	10.3147(2)	10.43833(16)
O4-cation	2.973(5)	3.024(5)	3.048(6)	2.957(7)
O6-cation	2.861(4)	2.837(4)	2.833(4)	2.937(5)
O1-cation	2.974(6)	2.983(6)	2.982(7)	2.931(8)
Angles / °				
δ	33.9(2)	33.1(2)	33.3(2)	25.0(3)

Table 3 S…S contacts shorter than the van der Waals distance for **I-IV**.

Salt	I	II	III
S1…S7	3.4023(13)	3.4257(13)	3.4393(16)
S3…S7	3.5452(13)	3.5322(13)	3.5261(15)
S2..S9	3.3715(14)	3.3550(14)	3.3507(17)
S2..S11	3.3992(13)	3.3884(13)	3.3939(17)
S6…S15	3.5200(13)	3.5190(13)	3.5205(17)
S8…S15	3.6089(16)	3.5893(16)	3.573(2)
Salt	**IV**		
S12…S13	3.481(2)		

S11…S14	3.506(2)		
S1…S12	3.294(2)		
S1…S10	3.531(2)		
S7…S16	3.449(2)		
S2…S9	3.568(2)		
S8…S15	3.566(2)		
S6…S9	3.562(2)		
S2…S13	3.499(2)		

Table 4 Average bond lengths (Å) in BEDT-TTF molecules for **I-IV** with approximation of the charge on the molecules. δ = (b+c)-(a+d), Q = 6.347-7.463δ.[22]



Salt	Donor	a	b	c	d	δ	Q
I	A	1.358	1.739	1.748	1.342	0.787	0.47
	B	1.365	1.735	1.748	1.343	0.775	0.56
II	A	1.358	1.738	1.747	1.347	0.780	0.53
	B	1.366	1.735	1.744	1.346	0.767	0.62
III	A	1.358	1.738	1.748	1.346	0.782	0.51
	B	1.370	1.735	1.749	1.341	0.773	0.58
IV	A	1.347	1.754	1.761	1.336	0.832	0.14
	B	1.389	1.721	1.741	1.351	0.722	0.96

Notes and references

†Electronic supplementary information (ESI) is available

‡ *Crystal data*: **I**: $C_{52}H_{40}F_1Rh_1O_{13}S_{32}$, M = 2020.90, black block, a = 10.32638(12), b = 19.9527(3), c = 35.0343(5) Å, β = 93.1002(12)°, U = 7207.87(10) Å^3, T = 294 K, space group *C2/c*, Z = 4, μ = 1.227 mm^{-1}, reflections collected = 24844, independent reflections = 7488, $R1$ = 0.0418, $wR2$ = 0.0813 [$F^2 > 2\sigma(F^2)$], $R1$ = 0.0451, $wR2$ = 0.0821 (all data).

Crystal data: **II**: $C_{52}H_{40}Cl_1Rh_1O_{13}S_{32}$, M = 2037.33, black block, a = 10.3180(3), b = 20.0233(4), c = 35.1173(6) Å, β = 93.5628(18)°, U = 7241.19(12) Å^3, T = 295 K, space group *C2/c*, Z = 4, μ = 1.256 mm^{-1}, reflections collected = 35653, independent reflections = 7754, $R1$ = 0.0452, $wR2$ = 0.0971 [$F^2 > 2\sigma(F^2)$], $R1$ = 0.0490, $wR2$ = 0.0990 (all data).

Crystal data: **III**: $C_{52}H_{41}Br_1N_1Rh_1O_{13}S_{32}$, M = 2080.82, black block, a = 10.3147(2), b = 20.0458(4), c = 35.2608(6) Å, β = 93.7457(17)°, U = 7275.18(12) Å^3, T = 294 K, space group *C2/c*, Z = 4, μ = 1.762 mm^{-1}, reflections collected = 35477, independent reflections = 7697, $R1$ = 0.0540, $wR2$ = 0.1035 [$F^2 > 2\sigma(F^2)$], $R1$ = 0.0602, $wR2$ = 0.1064 (all data).

Crystal data: **IV**: $C_{53}H_{41}N_2Rh_1O_{13}S_{32}$, M = 2026.93, black diamond, a = 10.43833(16), b =19.6739(3), c = 35.9215(6) Å, U = 7376.92(13) Å^3, T = 292 K, space group *Pbcn*, Z = 4, μ = 1.197 mm^{-1}, reflections collected = 60469, independent reflections = 8368, $R1$ = 0.0580, $wR2$ = 0.1272 [$F^2 > 2\sigma(F^2)$], $R1$ = 0.0596, $wR2$ = 0.1280 (all data).

§ CCDC 1536898-1536901 contains supplementary X-ray crystallographic data for **I-IV**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/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.

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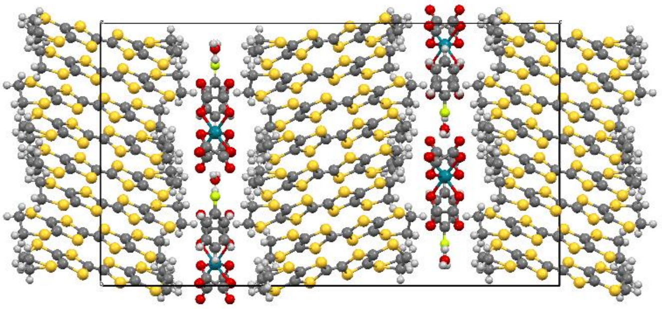

Fig. 1 View of the layered packing in the *a* direction in **I-III** showing the alternate organic donor layers and inorganic anionic layers.

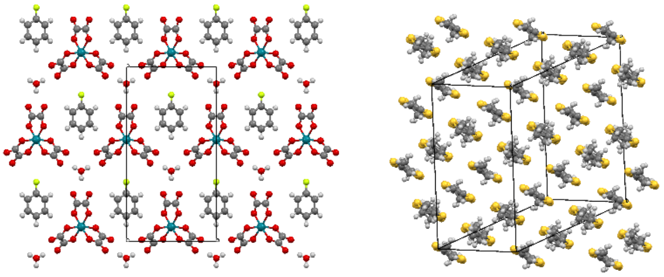

Fig. 2 Anion layer of **I-III** showing the honeycomb packing arrangement of the tris(oxalato)rhodate anions viewed down the *c* axis (left). β'' BEDT-TTF layer of **IV** viewed along the molecular long axis (right).

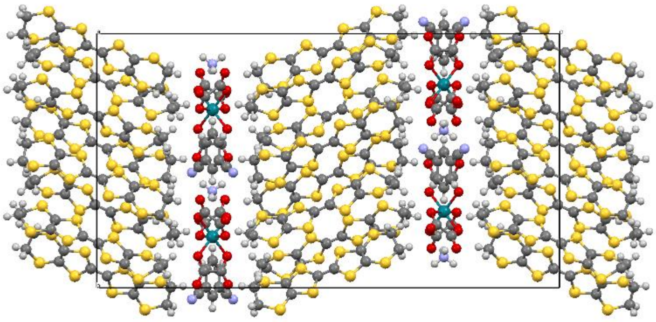

Fig. 3 View of the layered packing in the *a* direction in **IV** showing the alternate organic donor layers and inorganic anionic layers.

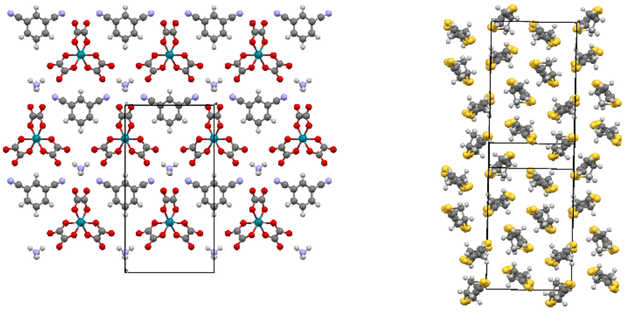

Fig. 4 Anion layer of **IV** showing the honeycomb packing arrangement of the tris(oxalato)rhodate anions viewed down the *c* axis (left). Pseudo-κ BEDT-TTF layer of **IV** viewed along the molecular long axis (right).

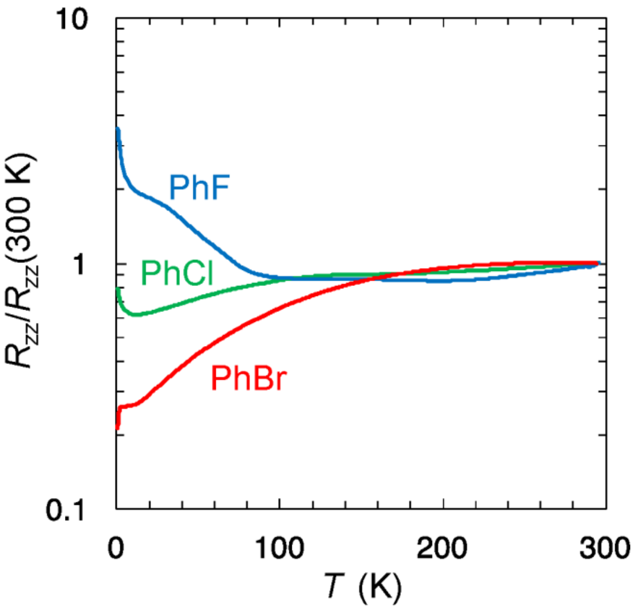

Fig. 5 Plot of resistance versus temperature for **I-III** from 300K to 0.8K.

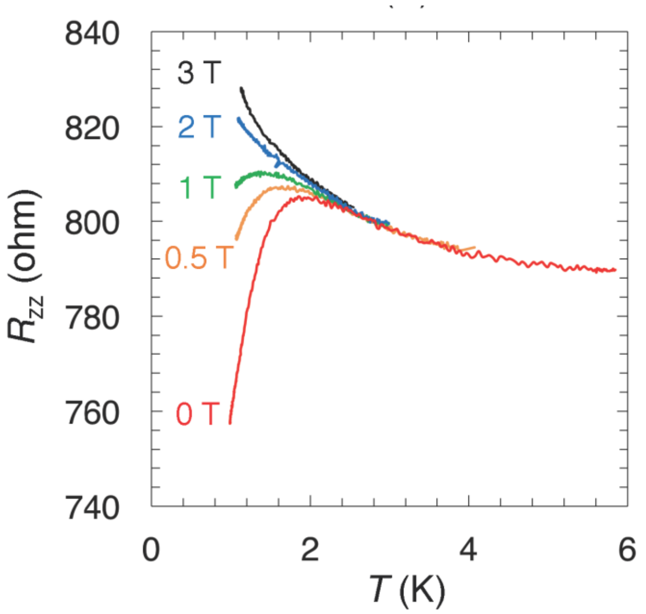

Fig. 6 Plot of resistance from 3K to 0.8K for **III** under different applied magnetic fields.

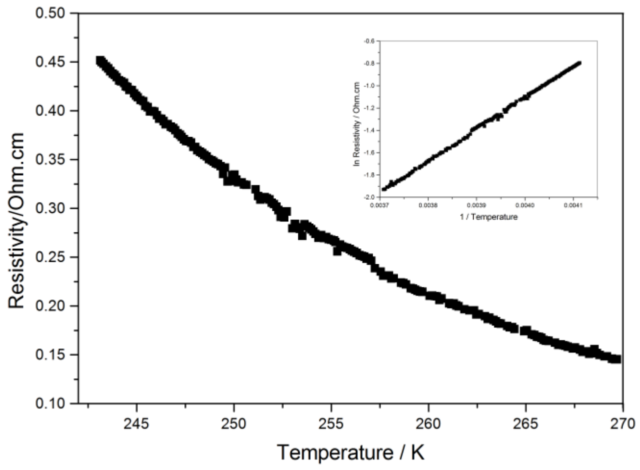

Fig. 7 Resistivity data for **IV** from 270 to 242K.