Bulk Kosterlitz-Thouless Type Molecular Superconductor β"-(BEDT-TTF)₂[(H₂O)(NH₄)₂Cr(C₂O₄)₃].18-crown-6

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ABSTRACT: A new molecular superconductor, β"-(BEDT-TTF)₂[(H₂O)(NH₄)₂Cr(C₂O₄)₃].18-crown-6, has been synthesized from the organic donor molecule BEDT-TTF with the anion $Cr(C_2O_4)_3^{3-}$. The crystal structure consists of conducting organic layers of BEDT-TTF molecules which adopt the β" packing motif (layer A), layers of NH_4^+ and Λ-Cr(C₂O₄)₃³⁻ (layer B), layers of (H₂O)(NH₄)18-crown-6 (layer C), and layers of NH_4^+ and Δ-Cr(C₂O₄)₃³⁻ (layer D) which produce a superstructure with a repeating pattern of ABCDABCDA. As a result of this packing arrangement this is the 2D superconductor with the widest gap between conducting layers where only a single donor packing motif is present (β"). Superconducting critical temperatures at ambient pressure observed by electrical transport and magnetic measurements are 4.0-4.9 and 2.5 K, respectively. The strong 2D nature of this system, the broad transition to T_{zero} at 1.8K, and the transition of α of $V \propto I^\alpha$ from 1 to 3 on I-V curves strongly suggests that the superconducting transition is very close to a Kosterlitz-Thouless transition. The magnetic field dependence of the superconducting critical temperature parallel to the conducting plane gives an upper critical field $\mu_0 H_{c2//} > 8$ T, which is over the calculated Pauli-Clogston limit for this material.

INTRODUCTION

The combination of magnetism and conductivity in the same multifunctional molecular material has long been a focus of new radical-cation salts of BEDT-TTF.[1] These materials provide the opportunity to investigate the competition and cooperation of multiple co-existing properties. Of the many paramagnetic anions used in the design of these materials the largest family, and the most extensively studied, are those employing tris(oxalato)metallate anions, $M(C_2O_4)_3^{x-}$. The family of BEDT-TTF radical-cation salts with tris(oxalato)metallate anions has produced paramagnetic superconductors,[2] antiferromagnetic semiconductors,[3] ferromagnetic metals,[4] and a proton-conducting metal[5] through small alterations to the formula or packing arrangement of the donors and anions.

The majority of salts in this family have the formula (BEDT-TTF)$_x$[(cation)M(C₂O₄)₃].guest (x = 3 or 4) with the donors and anions forming segregated stacks. The anion layer consists of a hexagonal network of $M(C_2O_4)_3^{x-}$ (M = Fe,[2,6] Cr,[7,8] Co,[7] Al,[7] Ga,[9] Ru,[10] Mn[11]) and cations (cation = H₃O⁺, K⁺, NH₄⁺,[6-11]). The honeycomb cavities are occupied by a guest electrolyte molecule, the size and shape of which influences the packing of the donor layer which in turn affects the conducting properties. Through subtle changes to the metal, cation, or electrolyte a wide variety of different packing arrangements of donor, and thus physical properties, have been reported.

The inclusion of smaller guest molecules and cations has also produced a 3:1 series having the formula (BEDT-TTF)₃[(cation)Metal³⁺(C₂O₄)₃].guest (cation = Li⁺, Na⁺, NH₄⁺; Metal = Fe,[12] Cr,[12-14] Al[14]). Larger guest phenyl molecules with bulky substituents can also occupy the hexagonal cavity protruding more on one side of the anion layer than the other to produce multi-layered 4:1 salts where adjacent donor layers each have a different packing type e.g. α-β"[15] or α-κ.[16]

Crown ethers are used to aid the dissolution of the tris(oxalato)metallate and there are two cases where 18-crown-6 is included in the radical-cation salt: α-(BEDT-TTF)₁₀(18-crown-6)₆K₆[Fe(C₂O₄)₃]₄(H₂O)₂₄,[17] and the metallic proton conductor β"-(BEDT-TTF)₄[(NH₄)M(C₂O₄)₃]₂.[(NH₄)₂(18-crown-6)].5H₂O[5] (M = Cr or Ga).

Despite the numerous phases that have been produced in the combination of BEDT-TTF with $M(C_2O_4)_3^{3-}$ over 20 years only the one superconducting phase is known: β"-(BEDT-TTF)₄[(cation)Metal³⁺(C₂O₄)₃].guest.[2] We report here the synthesis, crystal structure, electrical and magnetic properties of a new ambient-pressure superconductor which has the novel superlattice β"-(BEDT-TTF)₂[(H₂O)(NH₄)₂M(C₂O₄)₃].18-crown-6 (M = Cr, Rh).[18]

This new superconductor has a strong 2D nature. The broad transition from the onset of superconductivity to zero resistance, has led us to investigate the possibility of a Kosterlitz-Thouless transition in this system to explain the finite resistivity in the region $T_{zero}<T<T_c$ is originating

from flux flow of unbinding vortices and antivortices.[19] David J. Thouless, F. Duncan M. Haldane and J. Michael Kosterlitz were awarded the Nobel Prize for Physics in 2016 for their 'theoretical discoveries of topological phase transitions and topological phases of matter'.[20]

RESULTS AND DISCUSSION

Crystallising in triclinic space group $P\text{-}1$, β''-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Cr(C$_2$O$_4$)$_3$].18-crown-6 (**I**) has an asymmetric unit which consists of two crystallographically independent BEDT-TTF$^{0.5+}$ cations, one H$_2$O molecule, two NH$_4^+$ cations, one Cr(C$_2$O$_4$)$_3^{3-}$ anion and one 18-crown-6 molecule (Fig. 1).
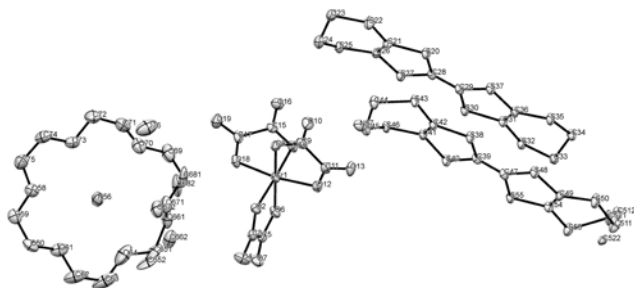

Fig. 1 ORTEP image of **I**.
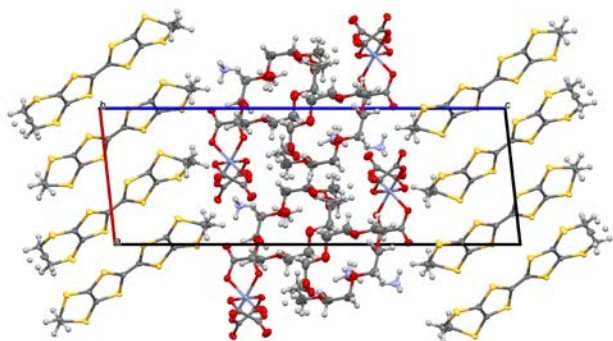
Fig. 2 Crystal structure of **I** viewed in the b direction showing alternating layers of BEDT-TTF, Λ-Cr(C$_2$O$_4$)$_3^{3-}$, 18-crown-6, and Δ-Cr(C$_2$O$_4$)$_3^{3-}$.
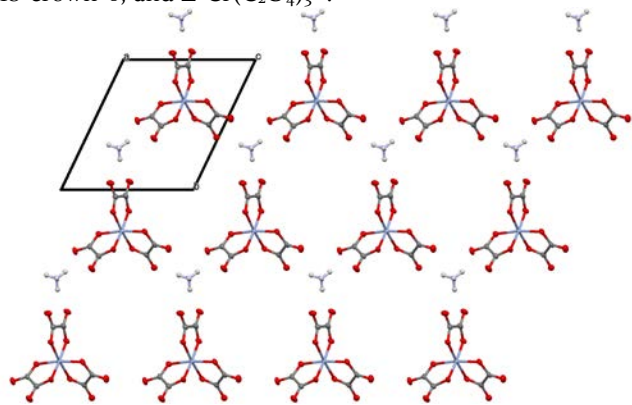
Fig. 3 Anion layer of **I** viewed in the c direction showing the hexagonal packing of the Cr(C$_2$O$_4$)$_3^{3-}$ anions and NH$_4^+$ cations.

The crystal structure of **I** consists of conducting organic layers of BEDT-TTF molecules which adopt the β'' packing motif (layer A), layers of NH$_4^+$ and Λ-Cr(C$_2$O$_4$)$_3^{3-}$ (layer B), layers of (H$_2$O)(NH$_4$)18-crown-6 (layer C), and layers of NH$_4^+$ and Δ-Cr(C$_2$O$_4$)$_3^{3-}$ (layer D) which produce a structure with a repeating pattern of ABCDABCDA (Fig. 2).

In the anion layers the NH$_4^+$ cations and Cr(C$_2$O$_4$)$_3^{3-}$ anions form a honeycomb network with hexagonal cavities (Fig. 3) similar to the paramagnetic superconducting family β''-(BEDT-TTF)$_4$[(A)M(C$_2$O$_4$)$_3$].Guest[2,6-9] where a solvent molecule from the electrocrystallisation is included in the salt. In salt **I** the electrocrystallisation solvents are not included in the salt and instead the 18-crown-6 molecules from the adjacent layer protrude into the cavities. A single 18-crown-6 molecule protrudes into the hexagonal cavity of only one adjacent anion layer (Fig. 4). At 110K the hexagonal cavity has dimensions of 6.28(1), 6.35(1), and 6.33(1) Å and a side-to-side width of 10.26(1) Å (area = 102.6(1) Å^2) (Table 1).

Table 1 Selected distances and angles for the anion layer of **I**.
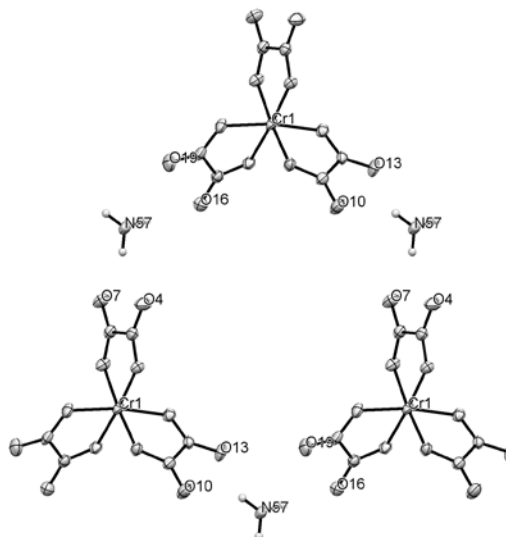
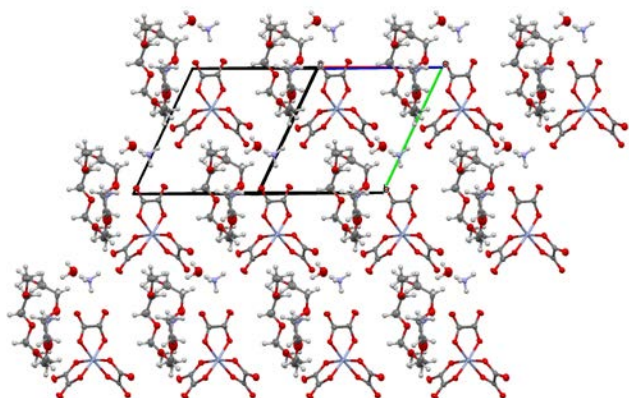|	Distances / Å
HEXAGON SIDES 6x Cr1 to N57	6.326(4) 6.353(5) 6.280(7)
HEXAGON HEIGHTS 3x Top Cr1 to bottom N57	13.654(5) 12.285(5) 11.841(7)
HEXAGON WIDTHS 3x Cr1 to Cr1 (or 3x N57 to N57)	11.3681(9) 11.1039(7) 10.2565(6)
Oxalate O4-cation N57	2.924(7)
Oxalate O7-cation N57	3.014(6)
Oxalate O10-cation N57	2.835(8)
Oxalate O13-cation N57	3.027(8)
Oxalate O16-cation N57	2.913(6)
Oxalate O19-cation N57	3.038(6)

Fig. 4 Anion layer of **I** showing the neighbouring crown ether molecules sited at the hexagonal cavities.
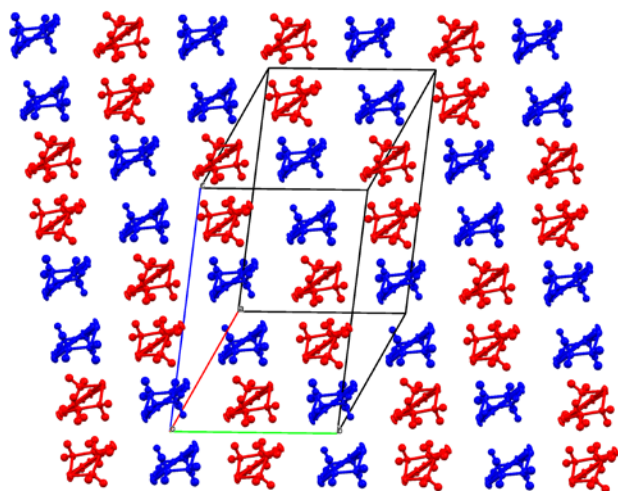

Fig. 5 BEDT-TTF layer of **I** viewed along the molecular long axis showing the β" packing motif. Donor A is shown in red, Donor B in blue.

Salt **I** has similar dimensions to superconductor β"-(BEDT-TTF)$_4$[(H$_3$O)Cr(C$_2$O$_4$)$_3$].benzonitrile which has hexagon sides 6.35(1), 6.28(1), and 6.35(1) Å and a width 10.24(1) Å at 120K (area = 102.2(1) Å^2).[6,7] Previous work has shown that the size of the hexagonal cavity does not depend on the size of the included guest molecule, but is dependent on the size of the M^{3+} and the distance from the outer oxalate oxygens to the cation K$^+$/NH$_4$$^+$/H$_3O^+$.[6]

The donor molecules adopt a β"-packing arrangement. The two crystallographically independent BEDT-TTF cations (A and B), follow a pattern of AABBAABB within a stack (Fig. 5). Donor A shows disorder of a terminal ethylene group at one end only at 110K, whilst the other donor is ordered. The disordered ethylene group is directed towards the NH$_4$$^+$ cation in the anion layer. Neighbouring BEDT-TTF layers are identical, unlike in other β" salts in this family where the planes of BEDT-TTFs in neighbouring layers are arranged approximately 65° to each other. There are numerous short sulphur-to-

sulphur contacts below the sum of the van der Waals radii in the range 3.246-3.550 Å (Table 2). All of these short contacts are side-to-side between BEDT-TTF molecules in adjacent stacks.

S...S	Distance / Å
S20...S35	3.540(2)
S25...S38	3.550(2)
S25..S43	3.521(3)
S30..S50	3.284(3)
S32...S50	3.246(3)
S46...S53	3.333(2)
S46...S55	3.453(2)

Table 2 S...S contacts shorter than the van der Waals distance for **I**.

Using the method of Guionneau et al.[21] (Table 3) it is estimated that all of the BEDT-TTF molecules have a charge of 0.5+ as expected for the formula β"-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Cr(C$_2$O$_4$)$_3$].18-crown-6.
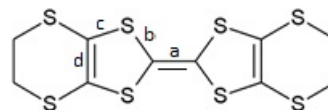
Donor	a / Å	b / Å	c / Å	d / Å	δ	Q
A	1.370	1.740	1.757	1.349	0.778	0.54$^+$
B	1.370	1.744	1.756	1.346	0.784	0.50$^+$

Table 3 Average bond lengths in BEDT-TTF molecules of **I** and approximation of charge on the molecules. $\delta = (b+c)-(a+d)$, $Q = 6.347-7.463\delta$.[22]

Magnetic susceptibility data collected on a polycrystalline sample at 0.1 T from 300 K to 5 K gives a Curie constant of 1.895 emu K mol^{-1} typical for a Cr^{3+} ion ($S = 3/2$) and a Weiss constant of 0.17 K indicates no interaction between Cr ions. Measurements at 2G showed the onset of the Meissner Effect at ~2.5 K (Fig. 6), and the Meissner volume at 1.7 K is calculated as 11.5%.

Temperature dependent electrical resistivity measurements were performed along the out-of-plane direction on single crystals of **I** down to 1K using the four probe method. The resistance decreases upon cooling with a downturn at ~4.2K for both in-plane and out-of-plane measurements indicating the onset of superconductivity (Fig. 7). The broad transition to T_{zero} at ~1.9 and 0.9 K for in-plane and out-of-plane measurements, respectively suggests a Kosterlitz-Thouless transition where T_{zero} means the temperature when the resistivity is likely to become zero, namely lower than the noise level (0.0004 mV at 10 μA in these measurements). In addition, the large difference of T_{zero} was likely caused by the sample dependence. At temperatures just above the superconducting transition there is no hump observed as can be seen in other examples of the β" BEDT-TTF-tris(oxalato)metallate family where resistivity begins to increase below a minimum at a temperature typically in the range 30-150K.[6]
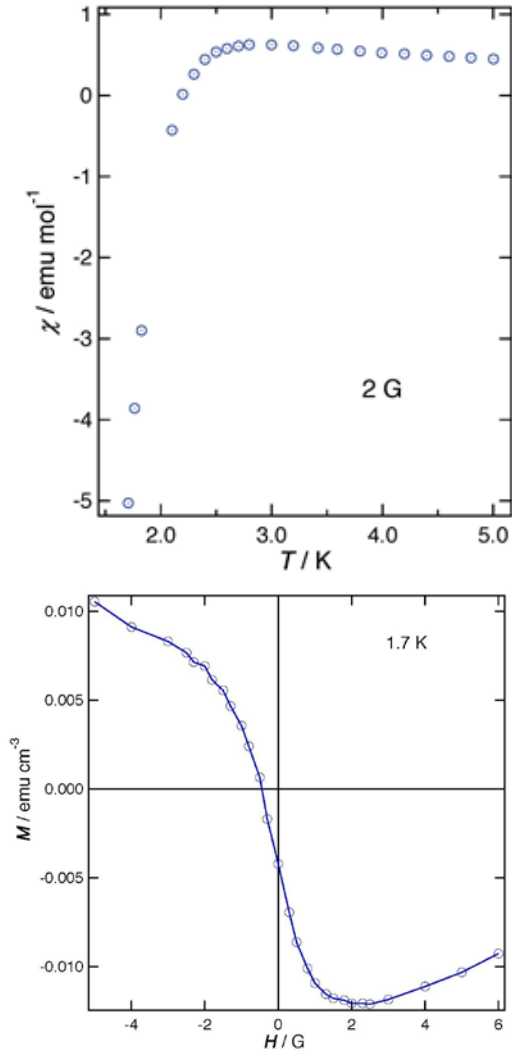
Fig. 6 Magnetic susceptibility for **I** at 2G showing onset of superconductivity at ~2.5K (top); magnetisation of **I** at 1.7 K at fields from -5 to 6 G (bottom). In addition, the magnet had approximately -0.4 G of remanent magnetization at this measurement.

The application of a magnetic field perpendicular or parallel to the conducting plane supresses the superconducting transition (Fig. 8). The magnetic field dependence of the superconducting critical temperature (Fig. 9) parallel to the conducting plane gives an upper critical field $\mu_0 H_{c2//} > 8$ T, which is over the calculated Pauli-Clogston limit for this material. Ginzburg-Landau coherence lengths are $\xi_{//} \sim 160$ Å and $\xi_\perp \sim 25$ Å, the latter of which was calculated using the lowest grade of the blue curve in Fig. 9 and the calculation using the steepest grade provide $\xi_\perp \sim 12$ Å, suggesting that the $\xi_\perp$ value is smaller than the length of c axis, which is evidence that the superconductivity has a perfect 2D nature.

The magnetic field dependence of the resistance shows Shubnikov-de Haas oscillations and Fermi liquid behaviour $\sim H^2$ (Fig. 10). The Fourier transform of the Shubnikov-de Haas oscillations show a small Fermi surface $F \sim 231.1 \pm 1.2$ T and a light effective mass $m^*/m \sim 1.4$.
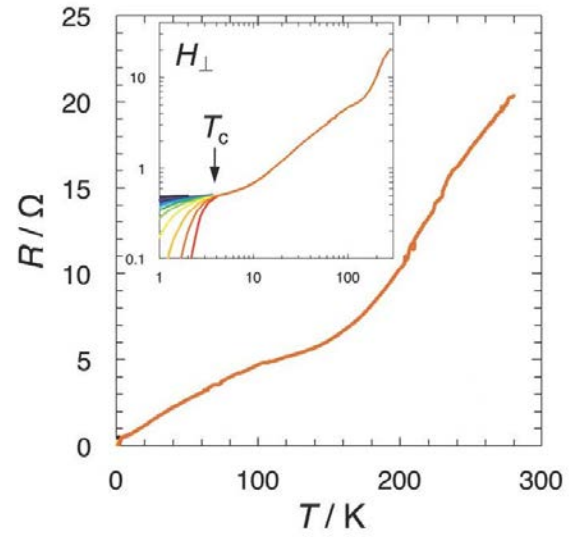

Fig. 7 Temperature dependence of resistance of **I** from room temperature to 1K. Onset of superconductivity is at ~4.2K, $T_{zero} \sim 1.8$K.
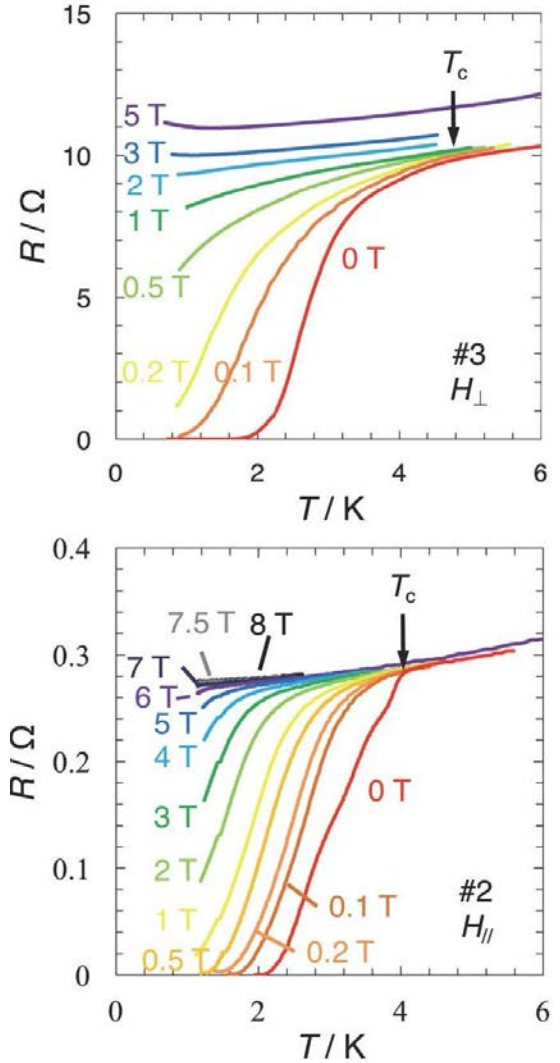

Fig. 8 Resistance of **I** under different magnetic fields applied perpendicular (top for Sample #3) or parallel (bottom for Sample #2) to the conduction plane.
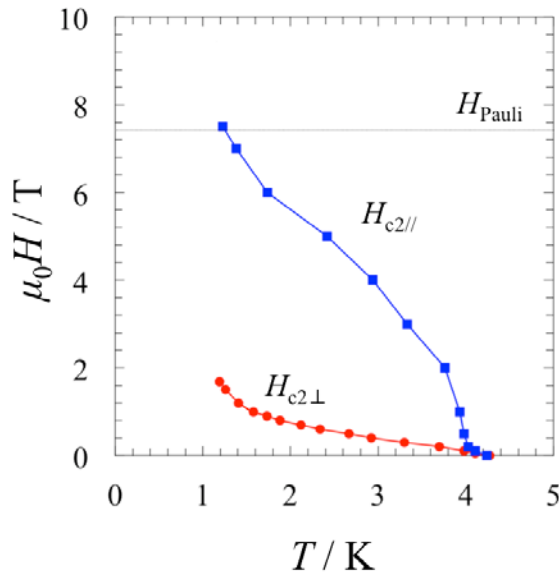
Fig. 9 Magnetic field dependence of the superconducting critical temperature (T_{onset}) both perpendicular and parallel to the conduction plane.
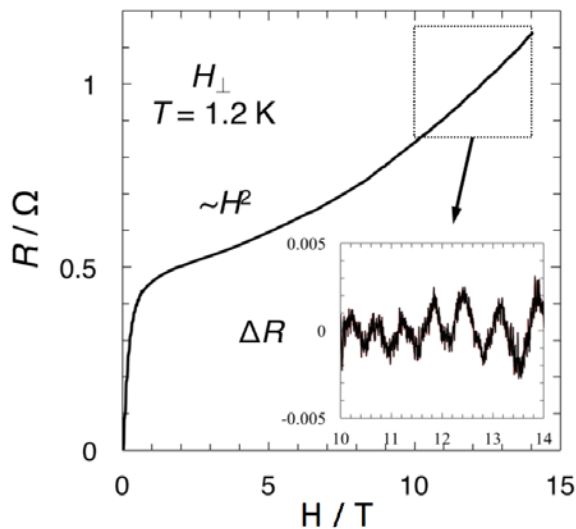

Fig. 10 Magnetic field dependence of the resistance at 1.2 K showing Shubnikov-de Haas oscillations.

We recently reported the isostructural superconducting salt from tris(oxalato)rhodate, β"-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Rh(C$_2$O$_4$)$_3$].18-crown-6. The T_c observed by transport measurement (T_{cT}) was 2.7 K and we were not able to observe zero resistivity. A T_c of 2.5 K was observed on the magnetization curve (T_{cM}), however, it was unclear and the Meissner signal was very small.

The results of the Rh salt are very different from those of the Cr salt. Zero resistivity for the Cr salt is clearly observed below 1.8 K and the Meissner signal is relatively large, although the transition is broader than those of normal superconducting salts and T_{cT} and T_{cM} differ greatly. It is somewhat strange because both Cr and Rh salts are isomorphous and the difference is very small. Here we discuss the reason why the large superconducting

property difference between the isomorphous Cr and Rh salts was observed. The ionic radii of Cr^{3+} and Rh^{3+} are 0.76 and 0.81 Å, respectively. Therefore the insulating layer of the Cr salt is likely to be thinner than that of the Rh salt. Actually the length of the c axis of the Cr salt of 27.3786(15) Å is 0.0553 Å shorter than that of the Rh salt of 27.4339(11) Å. This indicates that the Rh salt has larger gap between BEDT-TTF layers. In other words, the Rh salt has a stronger 2D nature. If the donor layer has a purely 2D nature the superconducting transition is a Kosterlitz-Thouless (KT) transition. We believe that the reason why the superconducting transition of the Rh salt is extraordinarily broad is because the strong 2D nature makes the transition become a KT transition. The transition is so broad that the extrapolation of the resistivity to 0 K is likely to give zero resistivity, which is evidence of a KT transition. Thus, it is a bulk KT superconducting transition. We at present believe that the Rh salt shows an almost perfect KT transition. On the other hand, the Cr salt shows a close to, but not perfect, KT transition so that we can observe zero resistivity and the large Meissner signal. This implies that the midpoint of the insulating layer's length between the Cr and Rh salt is a critical point of the perfect 2D nature. I-V character measurements below T_c for out-of-plane and in-plane directions are shown in Fig. 11a and 11b, respectively. Fig. 11c shows the α-V plots where the horizontal axis was scaled by $(T - T_{zero})/(T_c - T_{zero})$, which becomes zero at $T = T_{zero}$ and becomes 1 at $T = T_c$. The scaled in-plane curve is superinposed well to the out-of-plane one. The correspondence, a small jump of α of $V \propto I^\alpha$ from 1 to 3 (between dashed and dashdotted line) and the observation of T_{KT} (T at α = 3) at T_{zero} are definitely according to a theory of KT system.[22,23] In addition, the degree of two dimensionality, $\tau_c = (T_c - T_{KT})/T_c$ = 0.56-0.79 was estimated, which was much larger than that of bulk YBCO (0.0028)[24] and similar to that of single layer YBCO (0.63)[2]. The result indicates that the salt is almost perfect two dimensional system. If the salt is a more perfect KT superconductor, it should show a more clear jump. The I-V measurement of β"-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Rh(C$_2$O$_4$)$_3$].18-crown-6, which we believe is a more perfect bulk KT superconductor, is now in progress.

EXPERIMENTAL DETAILS

200 mg ammonium tris(oxalato)chromate and 250 mg 18-crown-6 ether dissolved in 10mL acetophenone:10mL 1,2,4-trichlorobenzene:1mL ethanol were placed in a two-compartment H-shaped electrochemical cell containing 10 mg ET in the anode compartment. A large quantity of black needle crystals were obtained upon applying a current of 1.0 µA across the cell for three weeks in a dark box on a vibration-free bench.

Crystal data: **I**: C$_{38}$H$_{50}$ O$_{19}$S$_{16}$N$_2$Cr$_1$, M = 1403.77, black needle, a = 10.2565(6), b = 11.1039(7), c = 27.3786(15) Å, α = 86.474(6), β = 82.734(6), γ = 64.165(5)°, U = 2783.3(3) Å^3, T = 110 K, space group *P-1*, Z = 2, μ = 0.878 mm^{-1}, reflections collected =

26682, independent reflections = 12672, $R1$ = 0.0718, $wR2$ = 0.1807 [$F^2 > 2\sigma(F^2)$], $R1$ = 0.0971, $wR2$ = 0.1951 (all data). CCDC 1561292 contains supplementary X-ray crystallographic data for **I**. 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.
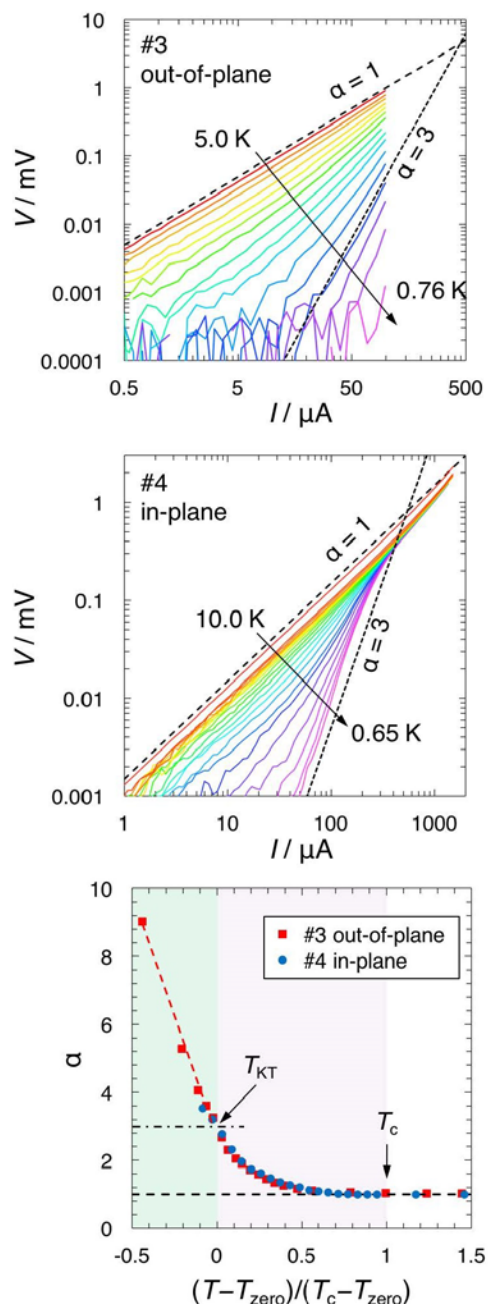

Fig. 11 *I-V* character for **I**. (a) Top and (b) middle figures show out-of-plane and in-plane measurements, respectively. (c) Bottom figure shows α-*I* plots where each α was obtained by the curvature of each *I-V* character in the $V \propto I^{\alpha}$ region.

CONCLUSIONS

The ambient-pressure superconductors β"-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$M(C$_2$O$_4$)$_3$].18-crown-6 (M = Cr, Rh) represent only the 2nd BEDT-TTF phase to show superconductivity with the tris(oxalato)metallate anion. It has a novel multilayered packing arrangement of BEDT-TTF, [M^{3+}(C$_2$O$_4$)$_3$]$^{3-}$ and 18-crown-6. This is the 2D superconductor with the widest gap between conducting layers where only a single donor packing motif is observed (β"). The evidence suggests that the Cr salt shows a close to perfect, and the Rh salt shows an absolutely perfect bulk Kosterlitz-Thouless transition.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes
The authors declare no competing financial interests.

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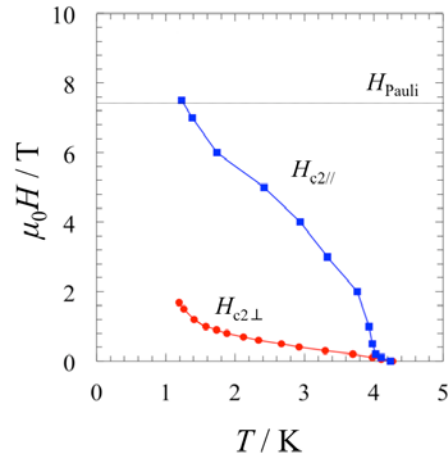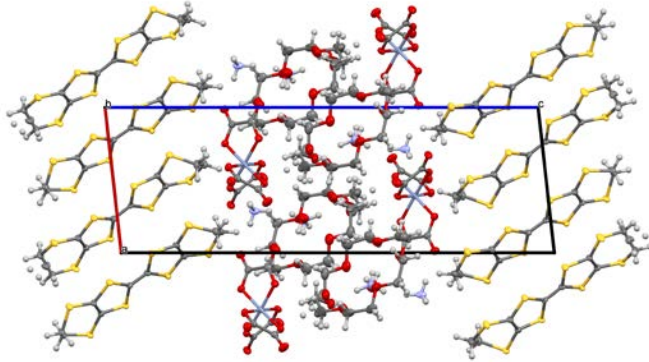
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A new molecular superconductor, β"-(BEDT-TTF)$_2$[(H$_2$O)(NH$_4$)$_2$Cr(C$_2$O$_4$)$_3$].18-crown-6, has been synthesized from the organic donor molecule BEDT-TTF with the anion Cr(C$_2$O$_4$)$_3^{3-}$. The crystal structure consists of conducting organic layers of BEDT-TTF molecules which adopt the β" packing motif (layer A), layers of NH$_4^+$ and Λ-Cr(C$_2$O$_4$)$_3^{3-}$ (layer B), layers of (H$_2$O)(NH$_4$)18-crown-6 (layer C), and layers of NH$_4^+$ and Δ-Cr(C$_2$O$_4$)$_3^{3-}$ (layer D) which produce a structure with a repeating pattern of ABCDABCDA. As a result of this packing arrangement this is the 2D superconductor with the widest gap between conducting layers where only a single donor packing motif is present (β"). Superconducting critical temperatures at ambient pressure observed by electrical transport and magnetic measurements are 4.0-4.9 and 2.5 K, respectively. The strong 2D nature of this system, the broad transition to T_{zero} at 1.8K, and the transition of α of $V \propto I^\alpha$ from 1 to 3 on *I-V* curves strongly suggests that the superconducting transition is very close to a Kosterlitz-Thouless transition. The magnetic field dependence of the superconducting critical temperature parallel to the conducting plane gives an upper critical field $\mu_0H_{c2//} > 8$ T, which is over the calculated Pauli-Clogston limit for this material.