

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

Lee Martin,^{†*} Jordan R. Lopez,[†] Hiroki Akutsu,[‡] Yasuhiro Nakazawa,[‡] and Shusaku Imajo[‡]

[†]School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS, United Kingdom.

[‡]Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan.

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(C₂O₄)₃³⁻. The crystal structure consists of conducting organic layers of BEDT-TTF molecules which adopt the β'' packing motif (layer A), layers of NH₄⁺ and Δ -Cr(C₂O₄)₃³⁻ (layer B), layers of (H₂O)(NH₄)₂18-crown-6 (layer C), and layers of NH₄⁺ and Δ -Cr(C₂O₄)₃³⁻ (layer D) which produce a superstructure with a repeating pattern of ABCDABCD. 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(C₂O₄)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 metal⁵ 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(C₂O₄)₃^{x-} (M = Fe,^{2,6} Cr,^{7,8} Co,⁷ Al,⁷ Ga,⁹ Ru,¹⁰ Mn¹¹) 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 Al¹⁴). 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)].5H₂O⁵ (M = Cr or Ga).

Despite the numerous phases that have been produced in the combination of BEDT-TTF with M(C₂O₄)₃³⁻ 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 $T_{\text{zero}} < T < T_c$ 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 $P\bar{1}$, β'' -(BEDT-TTF)₂[(H₂O)(NH₄)₂Cr(C₂O₄)₃].18-crown-6 (**I**) has an asymmetric unit which consists of two crystallographically independent BEDT-TTF^{0.5+} cations, one H₂O molecule, two NH₄⁺ cations, one Cr(C₂O₄)₃³⁻ anion and one 18-crown-6 molecule (Fig. 1).

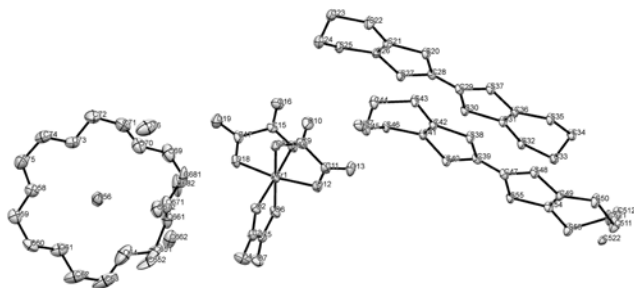


Fig. 1 ORTEP image of **I**.

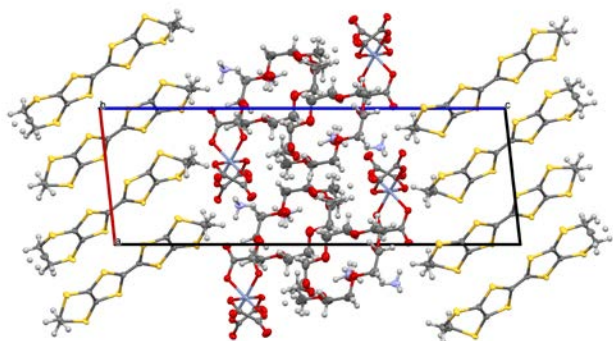


Fig. 2 Crystal structure of **I** viewed in the *b* direction showing alternating layers of BEDT-TTF, Λ -Cr(C₂O₄)₃³⁻, 18-crown-6, and Δ -Cr(C₂O₄)₃³⁻.

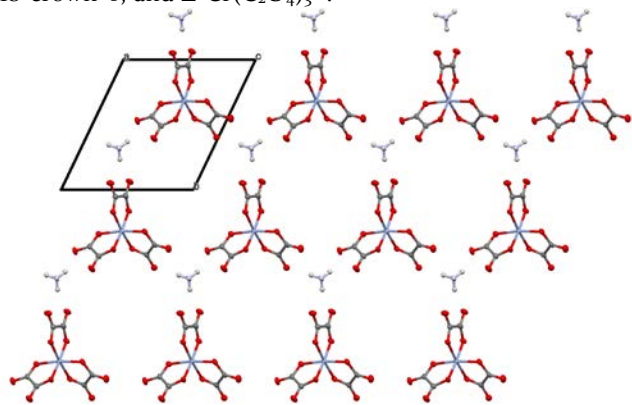
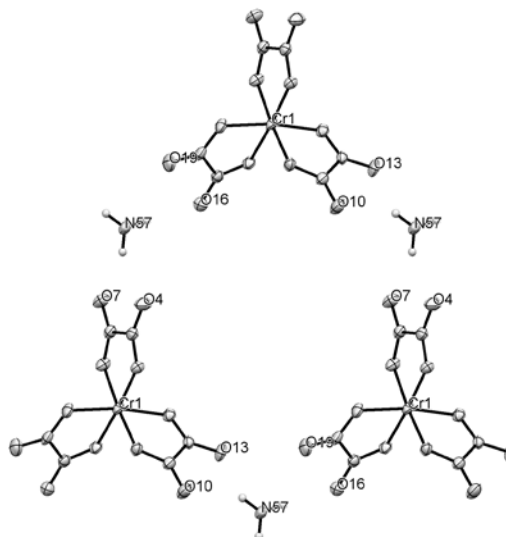


Fig. 3 Anion layer of **I** viewed in the *c* direction showing the hexagonal packing of the Cr(C₂O₄)₃³⁻ anions and NH₄⁺ cations.

The crystal structure of **I** consists of conducting organic layers of BEDT-TTF molecules which adopt the β'' packing motif (layer A), layers of NH₄⁺ and Λ -Cr(C₂O₄)₃³⁻ (layer B), layers of (H₂O)(NH₄)18-crown-6 (layer C), and layers of NH₄⁺ and Δ -Cr(C₂O₄)₃³⁻ (layer D) which produce a structure with a repeating pattern of ABCDABCD (Fig. 2).

In the anion layers the NH₄⁺ cations and Cr(C₂O₄)₃³⁻ anions form a honeycomb network with hexagonal cavities (Fig. 3) similar to the paramagnetic superconducting family β'' -(BEDT-TTF)₄[(A)M(C₂O₄)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) Å²) (Table 1).

Table 1 Selected distances and angles for the anion layer of **I**.



	Distances / Å
HEXAGON SIDES	6.326(4)
6x Cr1 to N57	6.353(5)
	6.280(7)
HEXAGON HEIGHTS	13.654(5)
3x Top Cr1 to bottom N57	12.285(5)
	11.841(7)
HEXAGON WIDTHS	11.3681(9)
3x Cr1 to Cr1	11.1039(7)
(or 3x N57 to N57)	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)

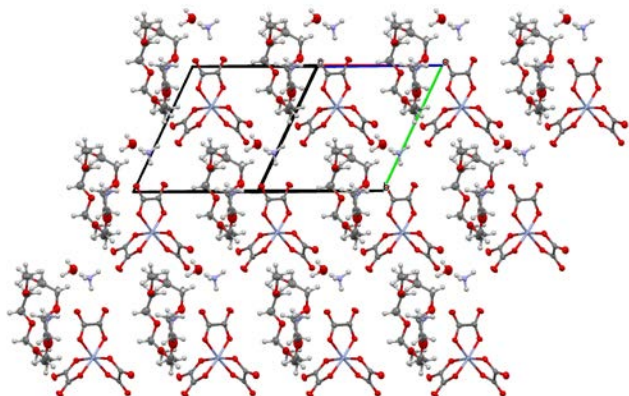


Fig. 4 Anion layer of I showing the neighbouring crown ether molecules sited at the hexagonal cavities.

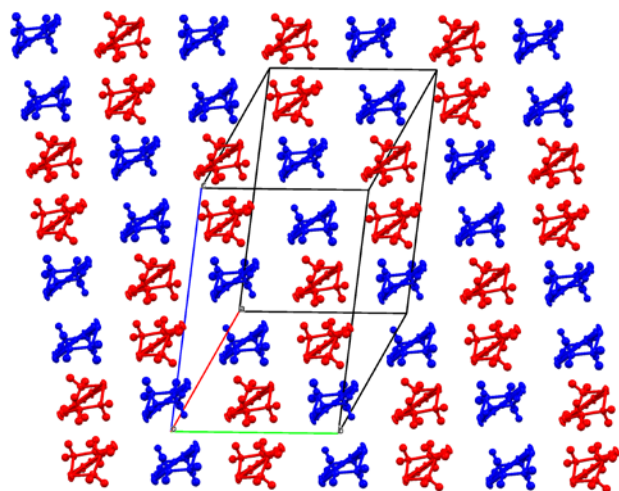


Fig. 5 BEDT-TTF layer of I viewed along the molecular long axis showing the β'' packing motif. Donor A is shown in red, Donor B in blue.

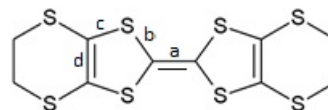
Salt I has similar dimensions to superconductor β'' -(BEDT-TTF)₄[(H₃O)Cr(C₂O₄)₃].benzotrifluoride which has hexagon sides 6.35(1), 6.28(1), and 6.35(1) Å and a width 10.24(1) Å at 120K (area = 102.2(1) Å²).^{6,7} Previous work has shown that the size of the hexagonal cavity does not depend on the size of the included guest molecule, but is dependent on the size of the M³⁺ and the distance from the outer oxalate oxygens to the cation K⁺/NH₄⁺/H₃O⁺.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 NH₄⁺ 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[(H₂O)(NH₄)₂Cr(C₂O₄)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 Cr³⁺ 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 μ A 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

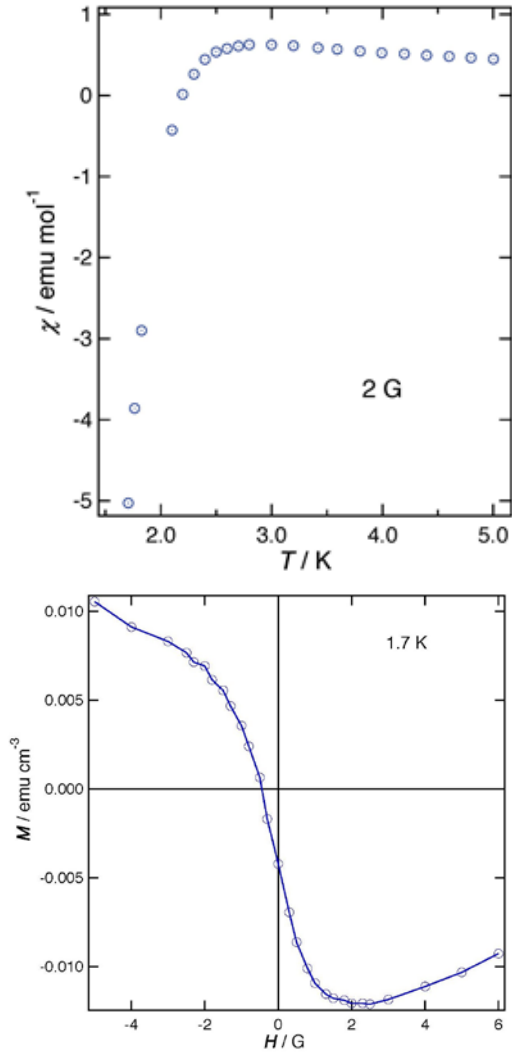


Fig. 6 Magnetic susceptibility for I at 2G showing onset of superconductivity at ~ 2.5 K (top); magnetisation of I at 1.7 K at fields from -5 to 6 G (bottom). In addition, the magnet had approximately -0.4 G of remanent magnetization at this measurement.

The application of a magnetic field perpendicular or parallel to the conducting plane suppresses 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 ξ_{\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 $m^*/m \sim 1.4$.

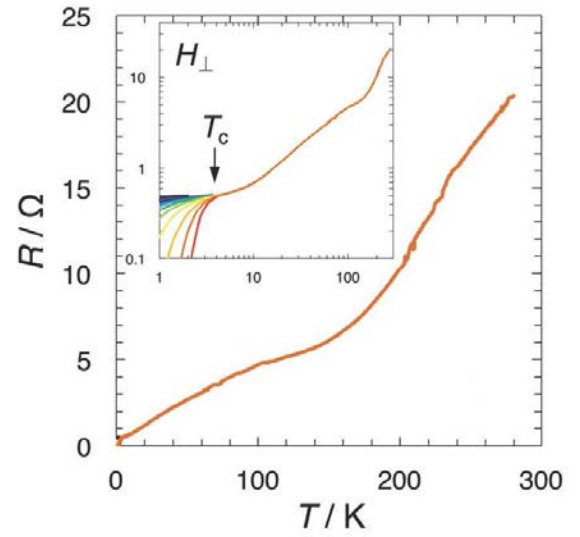


Fig. 7 Temperature dependence of resistance of I from room temperature to 1K. Onset of superconductivity is at ~ 4.2 K, $T_{\text{zero}} \sim 1.8$ K.

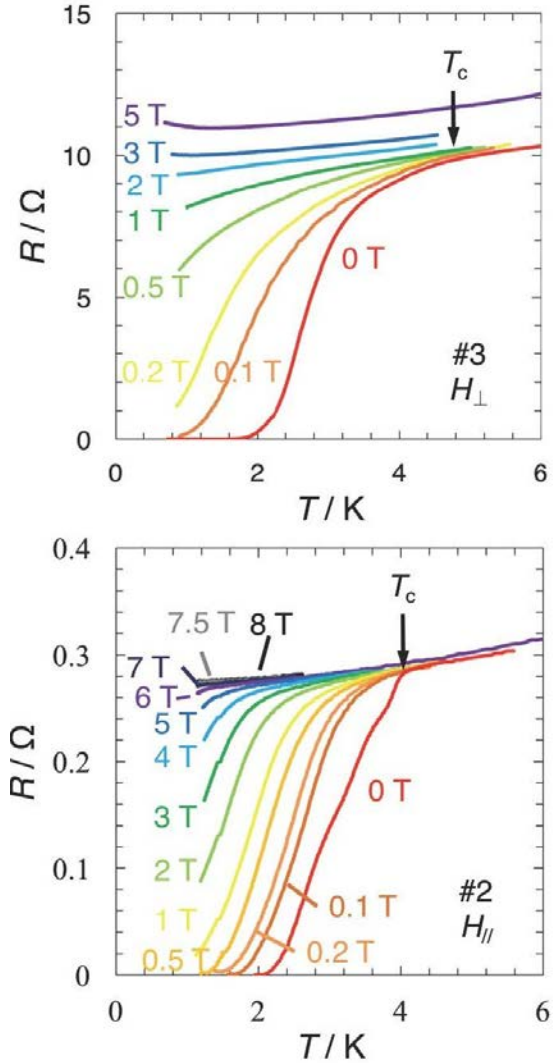


Fig. 8 Resistance of I under different magnetic fields applied perpendicular (top for Sample #3) or parallel (bottom for Sample #2) to the conduction plane.

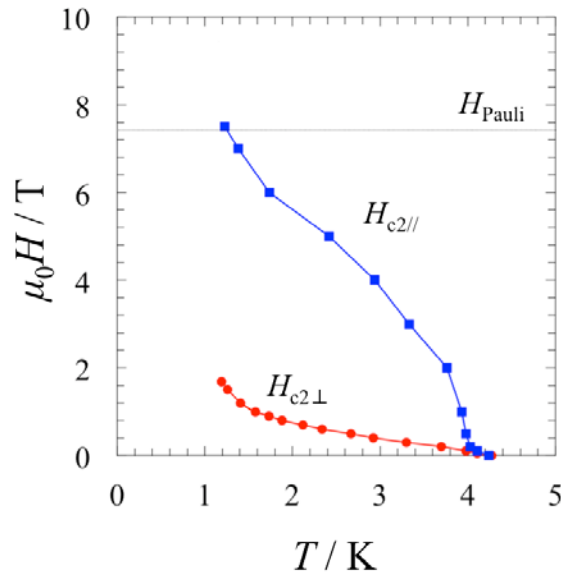


Fig. 9 Magnetic field dependence of the superconducting critical temperature (T_{onset}) both perpendicular and parallel to the conduction plane.

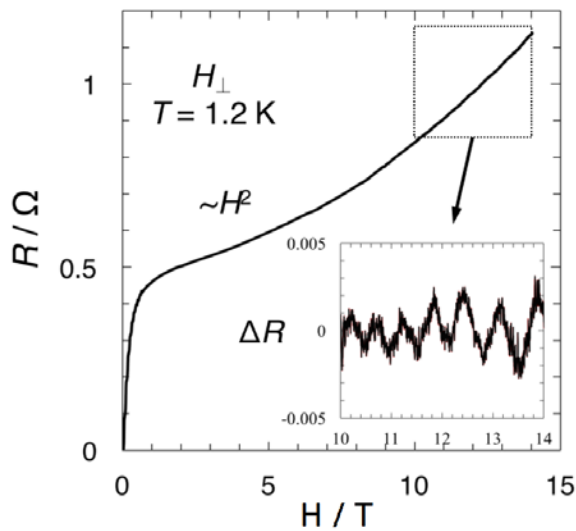


Fig. 10 Magnetic field dependence of the resistance at 1.2 K showing Shubnikov-de Haas oscillations.

We recently reported the isostructural superconducting salt from tris(oxalato)rhodate, β'' -(BEDT-TTF)₂[(H₂O)(NH₄)₂Rh(C₂O₄)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 Cr³⁺ and Rh³⁺ 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 $(T - T_{\text{zero}})/(T_c - T_{\text{zero}})$, which becomes zero at $T = T_{\text{zero}}$ and becomes 1 at $T = T_c$. The scaled in-plane curve is superimposed 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 $\alpha = 3$) 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[(H₂O)(NH₄)₂Rh(C₂O₄)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 μ A across the cell for three weeks in a dark box on a vibration-free bench.

Crystal data: I: C₃₈H₅₀ O₁₉S₁₆N₂Cr, $M = 1403.77$, black needle, $a = 10.2565(6)$, $b = 11.1039(7)$, $c = 27.3786(15)$ Å, $\alpha = 86.474(6)$, $\beta = 82.734(6)$, $\gamma = 64.165(5)^\circ$, $U = 2783.3(3)$ Å³, $T = 110$ K, space group *P*-1, $Z = 2$, $\mu = 0.878$ mm⁻¹, reflections collected =

26682, independent reflections = 12672, $R_1 = 0.0718$, $wR_2 = 0.1807$ [$F^2 > 2\sigma(F^2)$], $R_1 = 0.0971$, $wR_2 = 0.1951$ (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.

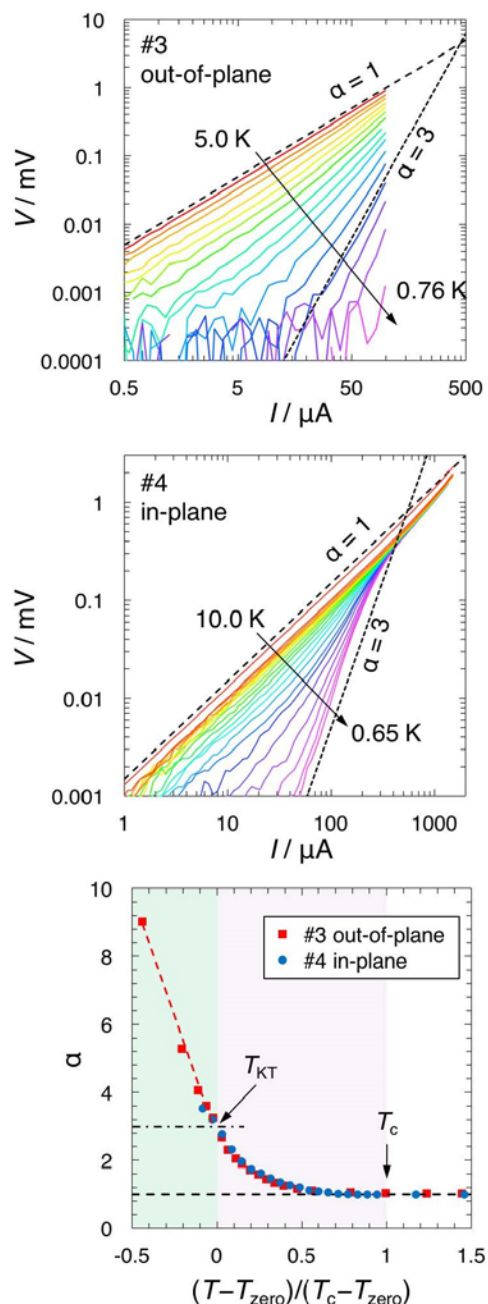


Fig. 11 I - V character for I. (a) Top and (b) middle figures show out-of-plane and in-plane measurements, respectively. (c) Bottom figure shows α - I plots where each α was obtained by the curvature of each I - V character in the $V \propto I^\alpha$ region.

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.

ACKNOWLEDGEMENT

JRL and LM would like to thank Nottingham Trent University for PhD funding.

AUTHOR INFORMATION

Corresponding Author

Email: lee.martin@ntu.ac.uk

Author Contributions

The manuscript was written through contributions of all authors.

Funding Sources

This work has been supported by JSPS [KAKENHI Grant Number JP17H01144] and Royal Society [Research Grants (RG100853 and RG081209), International Exchange Scheme (IE130367 and IE150152), and International Joint Project (JP0869972)].

Notes

The authors declare no competing financial interests.

REFERENCES

- 1 E. Coronado and P. Day, Magnetic Molecular Conductors, *Chem. Rev.*, 2004, 104, 5419-5448.
- 2 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, Superconducting and Semiconducting Magnetic Charge Transfer Salts: (BEDT-TTF) $_4$ AFe(C $_2$ O $_4$) $_3$ ·C $_6$ H $_5$ CN (A = H $_2$ O, K, NH $_4$), *J. Am. Chem. Soc.*, 1995, 117, 12209.
- 3 B. Zhang, Y. Zhang and D. Zhu, (BEDT-TTF) $_3$ Cu $_2$ (C $_2$ O $_4$) $_3$ (CH $_3$ OH) $_2$: an organic-inorganic hybrid antiferromagnetic semiconductor, *Chem. Commun.*, 2012, 48, 198-199.

- 4 E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García and V. Laukhin, Coexistence of ferromagnetism and metallic conductivity in a molecule-based layered compound, *Nature*, 2000, 408, 447.

- 5 A. Akutsu-Sato, H. Akutsu, S. S. Turner, P. Day, M. R. Probert, J. A. K. Howard, T. Akutagawa, S. Takeda, T. Nakamura and T. Mori, The First Proton-Conducting Metallic Ion-Radical Salts, *Angew.Chem.Int.Ed.*, 2005, **44**, 291.
- 6 (a) E. Coronado, S. Curreli, C. Giménez-Saiz, and C. J. Gómez-García, The Series of Molecular Conductors and Superconductors $ET_4[AFe(C_2O_4)_3] \cdot PhX$ ($ET = \text{bis(ethylenedithio)tetrathiafulvalene}$; $(C_2O_4)^{2-} = \text{oxalate}$; $A^+ = H_3O^+$, K^+ ; $X = F, Cl, Br, \text{ and } I$): Influence of the Halobenzene Guest Molecules on the Crystal Structure and Superconducting Properties, *Inorg. Chem.*, 2012, **51**, 1111–1126; (b) A. Akutsu-Sato, H. Akutsu, J.-i. Yamada, S.-i. Nakatsui, S. S. Turner and P. Day, Suppression of superconductivity in a molecular charge transfer salt by changing guest molecule: $\beta''\text{-(BEDT-TTF)}_4[(H_3O)Fe(C_2O_4)_3](C_6H_5CN)_x(C_5H_5N)_{1-x}$, *J. Mater. Chem.*, 2007, **17**, 2497–2499; (c) 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, Effect of electrocrystallization medium on quality, structural features, and conducting properties of single crystals of the $(BEDT-TTF)_4A^+[Fe^{III}(C_2O_4)_3] \cdot G$ family, *CrystEngComm*, 2011, **13**, 537–545; (d) S. S. Turner, P. Day, K. M. A. Malik, M. B. Hursthouse, S. J. Teat, E. J. MacLean, L. Martin and S. A. French, Effect of included solvent molecules on the physical properties of the paramagnetic charge transfer salts $\beta''\text{-(bedt-ttf)}_4[(H_3O)Fe(C_2O_4)_3] \cdot \text{solvent}$ ($\text{bedt-ttf} = \text{bis(ethylenedithio)tetrathiafulvalene}$), *Inorg. Chem.*, 1999, **38**, 3543–3549; (e) 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, New superconducting charge-transfer salts $(BEDT-TTF)_4[A \cdot M(C_2O_4)_3] \cdot C_6H_5NO_2$ ($A = H_3O$ or NH_4 , $M = Cr$ or Fe , $BEDT-TTF = \text{bis(ethylenedithio)tetrathiafulvalene}$), *J. Mater. Chem.*, 2001, **11**, 2095–2101; (f) S. Q. Sun, P. J. Wu, Q. C. Zhang and D. B. Zhu, The New Semiconducting Magnetic Charge Transfer Salt $(BEDT-TTF)_4 \cdot H_2O \cdot Fe(C_2O_4)_3 \cdot C_6H_5NO_2$: Crystal Structure and Physical Properties, *Mol. Cryst. Liq. Cryst.*, 1998, **319**, 259–269; (g) S. Q. Sun, P. J. Wu, Q. C. Zhang and D. B. Zhu, The new semiconducting magnetic charge transfer salt $(BEDT-TTF)_4 \cdot H_2O \cdot Fe(C_2O_4)_3 \cdot C_6H_5NO_2$: Crystal structure and physical properties, *Synth. Met.*, 1998, **94**, 161–166; (h) L. V. Zorina, T. G. Prokhorova, S. V. Simonov, S. S. Khasanov, R. P. Shibaeva, A. Manakov, V. N. Zverev, L. I. Buravov and E. B. Yagubskii, Structure and magnetotransport properties of the new quasi-two-dimensional molecular metal $\beta''\text{-(BEDT-TTF)}_4H_3O[Fe(C_2O_4)_3] \cdot C_6H_4Cl_2$, *J. Exp. Theor. Phys.*, 2008, **106**, 347–354; (i) E. Coronado, S. Curreli, C. Giménez-Saiz and C. J. Gómez-García, novel paramagnetic molecular superconductor formed by bis(ethylenedithio)tetrathiafulvalene, tris(oxalato) ferrate(III) anions and bromobenzene as guest molecule: $ET_4[(H_3O)Fe(C_2O_4)_3] \cdot C_6H_5Br$, *J. Mater. Chem.*, 2005, **15**, 1429–1436; (j) 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, Molecular Metals Based on BEDT-TTF Radical Cation Salts with Magnetic Metal Oxalates as Counterions: $\beta''\text{-(BEDT-TTF)}_4A[M(C_2O_4)_3] \cdot DMF$ ($A = NH_4^+$, K^+ ; $M = Cr^{III}$, Fe^{III}), *Adv. Funct. Mater.*, 2003, **13**, 403–411; (k) L. V. Zorina, S. S. Khasanov, S. V. Simonov, R. P. Shibaeva, P. O. Bulanchuk, V. N. Zverev, E. Canadell, T. G. Prokhorova and E. B. Yagubskii, Structural phase transition in the $\beta''\text{-(BEDT-TTF)}_4H_3O[Fe(C_2O_4)_3] \cdot G$ crystals (where G is a guest solvent molecule), *CrystEngComm*, 2012, **14**, 460–465; (l) A. Akutsu-Sato, A. Kobayashi, T. Mori, H. Akutsu, J.-i. Yamada, S.-i. Nakatsui, S. S. Turner, P. Day, D. E. Tocher, M. E. Light, M. B. Hursthouse, Structures and Physical Properties of New β' -BEDT-TTF Tris-Oxalatometallate (III) Salts Containing Chlorobenzene and Halomethane Guest Molecules, *Synth. Met.*, 2005, **152**, 373–376.
- 7 L. Martin, S. S. Turner, P. Day, P. Guionneau, J. A. K. Howard, D. E. Hibbs, M. E. Light, M. B. Hursthouse, M. Uruichi and K. Yakushi, Crystal Chemistry and Physical Properties of Superconducting and Semiconducting Charge Transfer Salts of the Type $(BEDT-TTF)_4[A^+M^{III}(C_2O_4)_3] \cdot PhCN$ ($A^+ = H_3O$, NH_4 , K ; $M^{III} = Cr, Fe, Co, Al$; $BEDT-TTF = \text{Bis(ethylenedithio)tetrathiafulvalene}$), *Inorg. Chem.*, 2001, **40**, 1363–1371.
- 8 L. Martin, S. S. Turner, P. Day, K. M. A. Malik, S. J. Coles and M. B. Hursthouse, Polymorphism based on molecular stereoisomerism in tris(oxalato) Cr(III) salts of bedt-ttf [bis(ethylenedithio)tetrathiafulvalene], *Chem. Commun.*, 1999, 513–514.
- 9 (a) H. Akutsu, A. Akutsu-Sato, S. S. Turner, D. Le Pevelen, P. Day, V. Laukhin, A. Klehe, J. Singleton, D. A. Tocher, M. R. Probert and J. A. K. Howard, Effect of included guest molecules on the normal state conductivity and superconductivity of $\beta''\text{-(}E_t[(H_3O)Ga(C_2O_4)_3] \cdot G$ ($G = \text{pyridine, nitrobenzene}$), *J. Am. Chem. Soc.*, 2002, **124**, 12430–12431; (b) T. G. Prokhorova, L. I. Buravov, E. B. Yagubskii, L. V. Zorina, S. V. Simonov, R. P. Shibaeva and V. N. Zverev, Metallic Bi- and Monolayered Radical Cation Salts Based on Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with the Tris(oxalato)gallate Anion, *Eur. J. Inorg. Chem.*, 2014, 3933–3940.
- 10 T. G. Prokhorova, L. V. Zorina, S. V. Simonov, V. N. Zverev, E. Canadell, R. P. Shibaeva and E. B. Yagubskii, The first molecular superconductor based on BEDT-TTF radical cation salt with paramagnetic tris(oxalato)ruthenate anion, *CrystEngComm*, 2013, **15**, 7048–7055.
- 11 S. Benmansour, Y. Sánchez-Máñez and C. J. Gómez-García, Mn-Containing Paramagnetic Conductors with Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), *Magnetochemistry*, 2017, **3**, 7.
- 12 L. Martin, H. Engelkamp, H. Akutsu, S.-i. Nakatsui, J.-i. Yamada, P. N. Horton and M. B. Hursthouse, Radical-cation salts of BEDT-TTF with lithium tris(oxalato)metallate(III), *Dalton Trans.*, 2015, **44**, 6219–6223.
- 13 (a) L. Martin, P. Day, S.-i. Nakatsui, J.-i. Yamada, H. Akutsu and P. N. Horton, A molecular charge transfer salt of BEDT-TTF containing a single enantiomer of tris(oxalato)chromate(III) crystallised from a chiral solvent, *CrystEngComm*, 2010, **12**, 1369–1372; (b) L. Martin, H. Akutsu, P. N. Horton and M. B. Hursthouse, Chirality in charge-transfer salts of BEDT-TTF of tris(oxalato)chromate(III), *CrystEngComm*, 2015, **17**, 2783–2790; (c) L. Martin, P. Day, P. N. Horton, S.-i. Nakatsui, J.-i. Yamada and H. Akutsu, Chiral conducting salts of BEDT-TTF containing a single enantiomer of tris(oxalato)chromate(III) crystallised from a chiral solvent, *J. Mater. Chem.*, 2010, **20**, 2738–2742.
- 14 L. Martin, H. Akutsu, P. N. Horton, M. B. Hursthouse, R. W. Harrington and W. Clegg, Chiral Radical-Cation Salts of BEDT-TTF Containing a Single Enantiomer of Tris(oxalato)aluminum(III) and -chromate(III), *Eur. J. Inorg. Chem.*, 2015, 1865–1870.
- 15 (a) H. Akutsu, A. Akutsu-Sato, S. S. Turner, P. Day, E. Canadell, S. Firth, R. J. H. Clark, J.-i. Yamada and S.-i. Nakatsui, Superstructures of donor packing arrangements in a series of molecular charge transfer salts, *Chem. Commun.*, 2004, 18–19; (b) L. Martin, P. Day, H. Akutsu, J.-i. Yamada, S.-i. Nakatsui, W. Clegg, R. W. Harrington, P. N. Horton, M. B. Hursthouse, P. McMillan, and S. Firth, Metallic molecular crystals containing chiral or racemic guest molecules, *CrystEngComm*, 2007, **9**, 865–867.
- 16 (a) T. G. Prokhorova, L. I. Buravov, E. B. Yagubskii, L. V. Zorina, S. V. Simonov, R. P. Shibaeva and V. N. Zverev, Metallic Bi- and Monolayered Radical Cation Salts Based on Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with the Tris(oxalato)gallate Anion, *Eur. J. Inorg. Chem.*, 2014, 3933–3940; (b) L. V. Zorina, S. S. Khasanov,

S. V. Simonov, R. P. Shibaeva, V. N. Zverev, E. Canadell, T. G. Prokhorova and E. B. Yagubskii, Coexistence of two donor packing motifs in the stable molecular metal α -pseudo- κ -(BEDT-TTF)₄(H₂O)[Fe(C₂O₄)₃]-C₆H₄Br₂, *CrystEngComm*, 2011, **13**, 2430–2438.

17 L. Martin, P. Day, W. Clegg, R. W. Harrington, P. N. Horton, A. Bingham, M. B. Hursthouse, P. McMillan and S. Firth, Multi-layered molecular charge-transfer salts containing alkali metal ions, *J. Mater. Chem.*, 2007, **17**, 3324–3329

18 L. Martin, A. L. Morrill, J. R. Lopez, H. Akutsu, Y. Nakazawa, S. Imajo and Y. Ihara, Ambient-pressure molecular superconductor with a superlattice containing layers of tris(oxalato)rhodate enantiomers and 18-crown-6, *Inorg. Chem.*, 2017, **56** (2), 717–720.

19 (a) J. M. Kosterlitz and D. J. Thouless, Long range order and metastability in two dimensional solids and superfluids. (Application of dislocation theory), *J. Phys. C: Solid State Phys.*, 1972, **5**, L124; (b) J. M. Kosterlitz and D. J. Thouless, Ordering, metastability and phase transitions in two-dimensional systems, *J. Phys. C: Solid State Phys.*, 1973, **6**, 1181; (c) J. M. Kosterlitz, The critical properties of the two-dimensional xy model, *J. Phys. C: Solid State Phys.*, 1974, **7**, 1046.

20 Physics Nobel Prize 2016
https://www.nobelprize.org/nobel_prizes/physics/laureates/2016/advanced.html (accessed 11th October 2017).

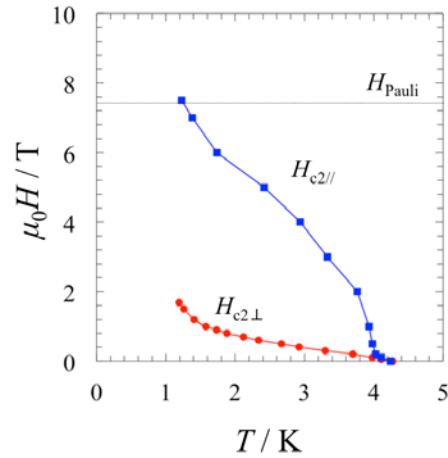
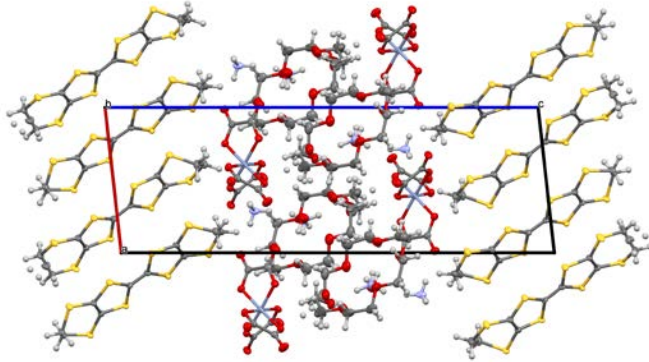
21 P. Guionneau, C. J. Kepert, D. Chasseau, M. R. Truter and P. Day, Determining the charge distribution in BEDT-TTF Salts, *Synth. Met.*, 1997, **86**, 1973.

22 D. J. Resnick, J. C. Garland, J. T. Boyd, S. Shoemaker, and R. S. Newrock, Kosterlitz-Thouless Transition in Proximity-Coupled Superconducting Arrays, *Phys. Rev. Lett.* 1981, **47**, 1542.

23 A. M. Kadin, K. Epstein, and A. M. Goldman, *Phys. Rev. B.*, 1983, **27**, 6691; P. Minnhagen, *Rev. Mod. Phys.*, 1987, **59**, 1001.

24 Y. Matsuda, S. Komiyama, T. Terashima, K. Shimura and Y. Bando, *Phys. Rev. Lett.*, 1992, **69**, 3228.

SYNOPSIS TOC



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(C₂O₄)₃³⁻. The crystal structure consists of conducting organic layers of BEDT-TTF molecules which adopt the β'' packing motif (layer A), layers of NH₄⁺ and Λ -Cr(C₂O₄)₃³⁻ (layer B), layers of (H₂O)(NH₄)18-crown-6 (layer C), and layers of NH₄⁺ and Δ -Cr(C₂O₄)₃³⁻ (layer D) which produce a structure with a repeating pattern of ABCDABCD. 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.
