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# The first molecular charge transfer salt containing proton channels

**Samina Rashid,[a] Scott S. Turner,[a] Peter Day,*[a] Mark E. Light,[b] Michael B. Hursthouse,[b] Steven Firth[c] and Robin J. H. Clark[c]**

[a] *Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1S 4BS. E-mail: pday@ri.ac.uk*
[b] *Department of Chemistry, University of Southampton, Southampton, UK SO17 1BJ*
[c] *Chemistry Department, University College London, 20 Gordon Street, London, UK WC1H 0AJ*

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**We report the first molecular charge transfer salt containing channels of $H_3O^+/H_2O$ within its lattice; it is formulated β″-(BEDT-TTF)$_4$[$(H_3O)Cr(C_2O_4)_3$]$_2$[$(H_3O)_2$(18-crown-6)]·$5H_2O$ [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene], deduced from the crystal structure and C=C and C–S bond lengths and Raman stretching frequencies.**

Molecular charge transfer salts based on organo-chalcogen donors, especially those containing bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have provided examples of most of the collective electronic ground states known to condensed matter science, such as semiconductors, metals, superconductors, antiferromagnets, spin-Peierls systems *etc.*[1] Because of their layered structures, in which organic donor cations and inorganic anions are segregated from one another (what we have called 'organic–inorganic composites' or 'chemically constructed multilayers'[2]), they are also a fruitful source of compounds combining two different types of functionality, like paramagnetic superconductors[3] or ferromagnetic metals.[4] However, with one exception,[5] there have been no reports of efforts to combine electronic with ionic conductivity in this class of compound. In that context we now report the first BEDT-TTF salt containing crown ether molecules and both $H_3O^+$ and $H_2O$ in the lattice, organised in such a way as to suggest the possibility of easy proton migration.

100 mg $(NH_4)_3[Cr(C_2O_4)_3]\cdot 3H_2O$, 200 mg 18-crown-6 ether, and 1 g pyrazine in a mixture of freshly distilled 25 ml of dichloromethane and 25 ml acetonitrile was stirred overnight, and filtered into an electrochemical cell. On applying a current of 1 μA across the cell, crystals first began to appear after 5 days and were harvested after 4 weeks. Two phases were obtained, long thin rectangular needles, whose structure was not resolved, and a small quantity of very thin dark brown plates. The structure of the latter was determined as β″-(BEDT-TTF)$_4$[$Cr(C_2O_4)_3$]$_2$·$C_{12}O_6H_{24}$·$9H_xO$ **1** (where $x$ = 2, 3). Single crystal X-ray diffraction data were collected using an Enraf Nonius Kappa CCD diffractometer mounted at the window of an Mo rotating anode generator with an Oxford Cryosystems $N_2$ open flow cryostat. The structure was solved by direct methods and refined anisotropically on $F^2$ using the SHELX97 program. H atoms were placed in idealised positions and refined using a riding model. Raman spectra were measured at room temperature with a Renishaw Ramascope System 1000 microscope equipped with a He–Ne laser (632.8 nm), using a slitwidth of 10 μm and a 10% neutral density filter.

Compound **1** crystallises in the triclinic space group $P\bar{1}$.† The structure consists of alternating layers of BEDT-TTF, and layers comprising $[Cr(C_2O_4)_3]^{3-}$, 18-crown-6 and water molecules. The packing of the layers follows the sequence ABCDABCDA, where A contains only BEDT-TTF, B contains $[Cr(C_2O_4)_3]^{3-}$ in either Δ or Λ configuration and an $H_3O^+$ molecule, as in the superconducting compound β″-(BEDT-TTF)$_4$[$(H_3O)Cr(C_2O_4)_3$]·PhCN,[6] while layer C contains the 18-crown-6 molecule and the remainder of the $H_xO$ molecules (where $x$ = 2, 3); layer D is a further $[(H_3O)Cr(C_2O_4)_3]^{2-}$ layer with the anions having opposite stereo-configuration to those in the B layer. Fig. 1 shows the packing of the successive layers projected onto the *bc* plane.

The BEDT-TTF molecules are arranged parallel to each other, in the β packing motif. There are two crystallographically independent BEDT-TTF molecules with similar charges of +0.4 ± 0.1 and +0.5 ± 0.1, as estimated from the C=C and C–S bond lengths,[7] which are close to those found in the β″-(BEDT-TTF)$_4$[$(H_3O)M(C_2O_4)_3$]·solv superconductors (solv being a solvent molecule). Since the $[Cr(C_2O_4)_3]^{3-}$ ions contribute a total charge of −6, this implies that four of the $H_xO$ molecules must be $H_3O^+$ to maintain charge neutrality. By analogy with the superconductors two of these may be located in layers B and D. The terminal $CH_2$–$CH_2$ groups of the BEDT-TTF are both twisted, with one of the C atoms above the plane of the TTF

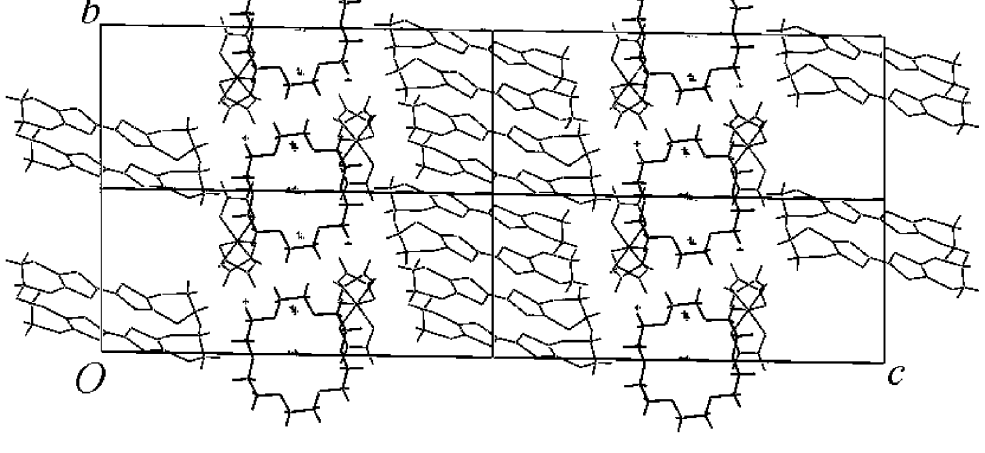

**Fig. 1** The crystal structure of **1** showing the overall packing of the cationic and anionic layers.

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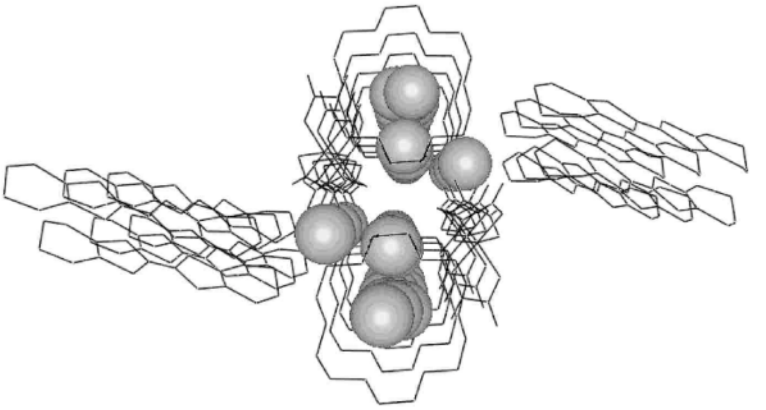

**Fig. 2** The crystal structure of **1** showing the channels formed by the 18-crown-6 molecules and $H_3O^+/H_2O$.

moiety and the other below, but eclipsed with respect to the other end of the donor molecule. The two shortest S···S contacts between the crystallographically independent BEDT-TTF molecules average to 3.70 Å, although these are longer than the S···S van der Waals distance of 3.6 Å. The torsion angles of the $CH_2$–$CH_2$ groups of the BEDT-TTF indicate that one of the groups on one of the molecules is under more strain than the others, and the thermal ellipsoids show that this $CH_2$–$CH_2$ group is disordered. In fact it is the one located directly next to the $Cr^{3+}$ centre of a tris(oxalato)Cr(III) ion. The other $CH_2$–$CH_2$ group, which has a more normal conformation, is closest to the 18-crown-6 ether.

Fig. 1 shows that, in contrast to the superconducting β″-BEDT-TTF tris(oxalato)metallate(III) salts,[8] the anion layer in **1** is almost as thick as two $[Cr(C_2O_4)_3]^{3-}$ and a molecule of 18-crown-6 ether. The latter separates the Δ and Λ forms of $[Cr(C_2O_4)_3]^{3-}$, between each of which there is one $H_3O^+$ cation, as in the superconducting phases. Thus there are two $[(H_3O)Cr(C_2O_4)_3]^{2-}$ layers, with crown ether and $H_xO$ layers between them. One water molecule resides within each molecule of crown ether, the other forming a H-bonded chain to the next crown ether molecule along the *a* axis. The O···O contacts between these four water molecules are 1.84, 1.97 and 1.47 Å, the latter appearing short because one of the O atoms is disordered over two sites. In this way the 18-crown-6 ether molecules form an ion channel within the inorganic layer, as shown in Fig. 2. In this figure the O atoms of $H_3O^+/H_2O$ are emphasised in space filling format, those on either side of the central chains being the $H_3O^+$ that form part of the $[(H_3O)Cr(C_2O_4)_3]^{2-}$ layers.

The Raman spectrum of **1** contains two peaks in the region of the totally symmetrical C=C vibrations at 1492 ± 2 and 1467 ± 2 $cm^{-1}$ corresponding to $\nu_3$ and $\nu_4$ of BEDT-TTF. From the established correlation between stretching frequency and cation charge,[9] charges of +0.54 and +0.46 are indicated, in close agreement with the charges indicated by the BEDT-TTF bond lengths in the crystal structure. On the assumption that the two anion layers B and D are formulated as $[(H_3O)Cr(C_2O_4)_3]^{2-}$ as in the superconducting phases, charge neutrality requires that two of the remaining seven $H_xO$ in the formula unit must be $H_3O^+$, the remaining five being $H_2O$. In the absence of evidence to the contrary, it can be assumed that the two $H_3O^+$ correspond to the water molecules closest to the rings of the crown ether molecules, with the remaining $H_2O$ forming a H-bonded channel between neighbouring crown ether rings as described above.

In conclusion, we have found a new kind of organic–inorganic layer architecture in a molecular charge transfer salt, in which layers of $BEDT\text{-}TTF^{0.5+}$ with the classical β″-stacking arrangement, are interleaved with two layers of $[(H_3O)Cr(C_2O_4)_3]^{2-}$ honeycomb layers. The latter have the same topology as in the paramagnetic superconductors β″-$(BEDT\text{-}TTF)_4[(H_3O)M(C_2O_4)_3]\cdot solv$[2,6,8,10] but in the present case, instead of alternate anion layers consisting exclusively either of Δ or Λ-$[Cr(C_2O_4)_3]^{3-}$ separated by BEDT-TTF layers, we find alternate $[(H_3O)Cr(C_2O_4)_3]^{2-}$, again with exclusively Δ or Λ stereo-configurations, but separated by crown ether/$H_3O^+/H_2O$ layers. The present small size and fragility of the crystals has inhibited detailed variable temperature transport measurements. However, a preliminary two-probe room temperature measurement gave a conductivity of 0.95 S $cm^{-1}$ parallel to the plate long axis, which is in the range expected for a semiconductor. We could expect that four-probe measurements, where the contact resistances are discounted, would be higher and even metallic in nature like other β″-BEDT-TTF salts. Therefore, the possibility exists to combine both electronic and ionic conductivity in a molecular lattice which is important in fields as diverse as solid-state batteries[11] and electroluminescent displays.[12]

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## Notes and references

† *Crystal data*: β″-$(BEDT\text{-}TTF)_4[Cr(C_2O_4)_3]_2\cdot C_{12}H_{24}O_6\cdot 9H_xO$ ($x$ = 2 or 3) $C_{32}H_{33}CrO_{19}S_{16}$, $M$ = 1289.50, triclinic, space group $P\bar{1}$, $a$ = 10.2212(5), $b$ = 11.2266(5), $c$ = 20.0998(15) Å, $\alpha$ = 88.433(3), $\beta$ = 88.391(2), $\gamma$ = 63.780(3)°, $V$ = 2479.6(2) Å$^3$, $T$ = 150 K, $Z$ = 2; $\lambda$ (Mo-K$\alpha$) = 0.71073 Å $\mu$ = 0.973 $mm^{-1}$, reflections collected 19985, independent reflections 8722, final $R$ indices $[F^2 > 2\sigma(F^2)]$: $R_1$ = 0.0605, $wR_2$ = 0.1222.

CCDC reference number 166475. See http://www.rsc.org/suppdata/cc/b1/b103877j/ for crystallograpic data in CIF or other electronic format.

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