β''-(BEDT-TTF)$_4$[(H$_3$O)Cr(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$: Effect of Included Solvent on the Structure and Properties of a Conducting Molecular Charge-Transfer Salt

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Among the numerous superconducting charge-transfer salts formed by the organo-chalcogen donor bis(ethylenedithio)-tetrathiafulvalene, BEDT-TTF, those containing tris(oxalato)-metalate(III) anions have been of special interest for two reasons. First, they provided the earliest examples of molecular superconductors incorporating paramagnetic metal centers within their lattices, and the first superconductors of any kind containing paramagnetic 3d ions.[1,2] A ferromagnetic metallic phase has also been reported.[3] Second, their properties turn out to be highly sensitive to the nature of solvent molecules incorporated in the crystal. For example, when the general formula for the series is written as β''-(BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]S, superconductors have been identified for A = H$_3$O, M = Cr, Fe, and S = PhCN,[2,4] PhNO$_2$,[5] although the T_c values of the PhNO$_2$ adducts are only about 60% of those in the PhCN ones with corresponding M. Furthermore, when A = H$_3$O, M = Fe, and S = C$_5$H$_5$N,[6] there is instead a metal−insulator transition at 116 K. The crystal structures of all the paramagnetic compounds are very closely related layers of stacked BEDT-TTF molecules alternating with hexagonal honeycomb layers of [M(C$_2$O$_4$)$_3$]$^{3-}$ and H$_3$O$^+$. The solvent molecules reside within hexagonal cavities in the latter layer, with their aromatic rings aligned at about 30° to the plane of the layer. In the case of the pyridine adduct, one terminal ethylene group of BEDT-TTF, lying above the solvent molecule, is disordered with an unusual boat conformation, which may account for the contrasting low-temperature properties. Given that the cavity occupied by the solvent molecule is hexagonal, it might be thought that the aromatic rings play a templating role in stabilizing the crystal structure. However, we now report the crystal structure and physical properties of a further member of this series in which the cavity is occupied only by CH$_2$Cl$_2$. While this new compound is metallic close to room temperature, it has a very broad transition below 150 K to activated conductivity, although not with the temperature dependence of a conventional semiconductor. As in the pyridine adduct, the CH$_2$Cl$_2$ solvate exhibits disorder in the donor layer.

Table 1. Crystal and Refinement Data for β''-(BEDT-TTF)$_4$[(H$_3$O)Cr(C$_2$O$_4$)$_3$]·CH$_2$Cl$_2$

chem formula	C$_{47}$H$_{37}$CrO$_{13}$S$_{32}$Cl$_2$	space group	$C2/c$ (No. 15)
a, Å	10.2800(4)	T, K	150(2)
b, Å	19.7144(11)	λ, Å	0.710 73 (Mo Kα)
c, Å	34.7368(19)	ρ_{calcd}, g cm^{-3}	1.851
β, deg	93.858(10)	μ, cm^{-1}	12.50
V, Å^3	7023.9	$R(F_o{}^2)^a$	0.0506
Z	8	$R_w(F_o{}^2)^b$	0.1050
fw	2027.76		

^{a} $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. ^{b} $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Experimental Section

A 100 mg portion of (NH$_4$)$_3$[Cr(C$_2$O$_4$)$_3$]·3H$_2$O, 200 mg of 18-crown-6, and 1 g of 2-chloropyridine in a mixture of 25 mL of freshly distilled dichloromethane and 25 mL of acetonitrile was stirred overnight, and the solution was filtered into an electrochemical H-shaped cell. When a current of 1 μA was applied across the cell, a few very thin dark brown plates first appeared after 5 days and were harvested after 4 weeks. When an identical mixture, but without the 2-chloropyridine, was used under the same conditions, no crystals formed.

The crystal structure of the brown plates was solved from X-ray diffraction data collected at 150 K on an Enraf-Nonius Kappa CCD diffractometer with Mo Kα radiation and an Oxford Instruments N$_2$ open flow cryostat. The structure was solved by direct methods and refined anisotropically on F using the CRYSTALS program.[7] All H atoms except those of H$_3$O$^+$ were placed in idealized positions and refined using a riding model. Magnetic susceptibility of a polycrystalline sample was measured from 300 to 2 K using a Quantum Design MPMS7 SQUID magnetometer. Variable-temperature four-probe dc conductivity measurements employed Pt paint (Degussa) contacts and an Oxford Instruments Maglab 2000 cryostat with an EP probe. Measurements were performed on a single crystal shaped as a flat thin rectangular sheet. The conductivity was measured along one axis only (parallel to the c axis), and measurements were made from 300 to 2 K on cooling at a rate of 1 K per minute. 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 slit width of 10 μm and a 10% neutral density filter.

Results and Discussion

β''-(BEDT-TTF)$_4$[(H$_3$O)Cr(C$_2$O$_4$)$_3$]·CH$_2$Cl$_2$ (**1**) crystallizes in the monoclinic space group $C2/c$. The crystal structure was solved at 150 K, and Table 1 contains the relevant crystallographic data and collection parameters. Figure 1 shows a standard ORTEP diagram of the structure with 50% thermal ellipsoids and atom numbering scheme. Disorder can be seen on the solvent molecule, CH$_2$Cl$_2$, and on one of the terminal CH$_2$CH$_2$ groups on the BEDT-TTF molecule labeled A.

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(1) Graham, A. W.; Kurmoo, M.; Day, P. *J. Chem. Soc., Chem. Commun.* **1995**, 2061.
(2) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209.
(3) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, L. V. *Nature* **2000**, *408*, 447.
(4) Martin, L.; Turner, S. S.; Day, P.; Mabbs, F. E.; McInnes, E. J. L. *J. Chem. Soc., Chem. Commun*. **1997**, 1367.
(5) Rashid, S.; Turner, S. S.; Day, P.; Howard, J. A. K.; Guionneau, P.; McInnes, E. J. L.; Mabbs, F. E.; Clark, R. J. H.; Firth, S.; Biggs, T. *J. Mater. Chem.* **2001**, *11*, 2293.
(6) Turner, S. S.; Day, P.; Malik, K. M. A.; Hursthouse, M. B. *Inorg. Chem.* **1999**, *38*, 3543.
(7) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, R. I. Crystals 2000, issue 11; Chemical Crystallography Laboratory, Oxford, U.K., 1999.

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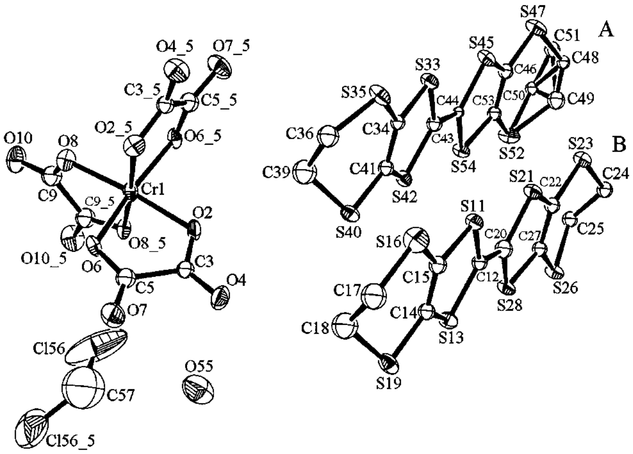

Figure 1. ORTEP[10] diagram showing 50% thermal ellipsoids and atom labeling of **1**. H atoms have been removed for clarity.

In the asymmetric unit there are two crystallographically independent BEDT-TTF molecules with similar positive charges of +0.5(1) and +0.6(1), as estimated from the bond lengths using the relationship of Guionneau et al.[8] The β'' stacking motif is identical with that found in the superconducting PhCN and $PhNO_2$ salts. In contrast to the CH_2CH_2 groups on the BEDT-TTF molecule A, those on molecule B are both in the twisted conformation, with one carbon atom of the CH_2CH_2 groups above the molecular plane and the other below. The two terminal groups of molecule B are eclipsed with respect to each other, as in the superconducting phases. The terminal CH_2CH_2 groups on molecule A are disordered between two orientations, corresponding to partial occupancies of the atoms C48, C51 and C49, C50. The latter CH_2CH_2 group lies in a void between the solvent molecule, two tris(oxalato)metalate(III) anions, and the H_3O^+ ion. It therefore penetrates into the anion layer, forming weak H bonds with the tris(oxalato)metalate(III) anions and H_3O^+ (Figure 2). The CH_2CH_2 group at the other end of the BEDT-TTF molecule A also lies in a void within the hexagonal cavity but further away from the tris(oxalato)metalate(III) anions. The positional parameters of the H atoms of the BEDT-TTF were not refined, but calculated positions were used to estimate the closest contacts between the terminal CH_2CH_2 H atoms and the inorganic layer, as listed in Table 2. At 150 K there are several short S···S contacts between BEDT-TTF molecules (S26···S47, 3.34(4) Å; S28···S47, 3.32(4) Å; S40···S52, 3.39(4) Å; S19···S33, 3.44(4) Å; S19···S35, 3.50(4) Å; S40···S54, 3.57(4) Å). In addition there is just one short face-to-face contact S19···S52 at 3.59(4) Å, slightly below the S···S van der Waals distance. For the corresponding Cr salts with other solvents the shortest S···S contacts are approximately equal for the CH_2Cl_2 (3.32(4) Å), $PhNO_2$ (3.31(1) Å), and PhCN (3.31(1) Å) solvates, with the C_6H_5N solvate (unpublished data) having a slightly longer value (3.36(4) Å).

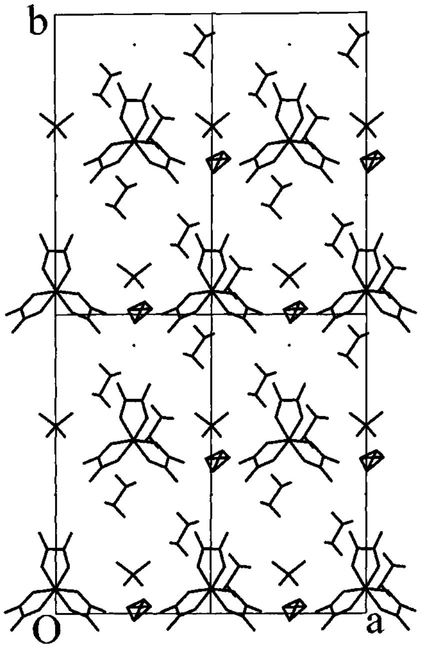

Figure 2. Docking of BEDT-TTF with the $[(H_3O)Cr(C_2O_4)_3]$ layer in **1**, showing the ordered and disordered terminal ethylene groups of the donor and the CH_2Cl_2.

Table 2. Close Contacts (Å) between the BEDT-TTF Hydrogen Atoms and $[Cr(C_2O_4)_3]^{3-}$ O Atoms in 1

BEDT-TTF A[a]			
H48-1−O7	2.38	H50-2−O4	2.50
H49-1−O4	2.43	H48-1−C5	3.24
BEDT-TTF B[a]			
H39-2−O2	2.30	H18-2−O55	3.02
H18-1−O4	2.65	H18-2−O4	3.09

[a] The proton numbering refers to the C atom to which the H is attached.

The inorganic layer comprises an approximately hexagonal network formed by the chiral $[M(C_2O_4)_3]^{3-}$ and H_3O^+ ions. The average distance between the O atoms of H_3O^+ and oxalate is 2.9 Å, indicating a H-bonding interaction between the two. As in the members of this series of salts containing PhCN and $PhNO_2$, the presence of H_3O^+ rather than H_2O is indicated by calculating the BEDT-TTF charge from its bond lengths.[8] The Cr atoms are octahedrally coordinated to the oxalate ligands, conferring D_3 symmetry on the metal center, and alternate anion layers are comprised exclusively either of Δ or Λ stereoisomers.

The CH_2Cl_2 molecule sits in the lower portion of the hexagonal cavity formed by three $[Cr(C_2O_4)_3]^{3-}$ units with the C atom closer to H_3O^+ (C57−O55 distance 4.54 Å) than to the tris(oxalato)metalate(III) anion (C57−Cr1 distance 8.9 Å). As expected, the area of the hexagonal cavity, measured by using Cr and O (of H_3O) as apexes, is smaller than those observed in the corresponding Cr compounds that contain larger included molecules. The order of the cavity sizes for the solvates is CH_2Cl_2 (101.3 Å^2) < C_6H_5N (102.1 Å^2) < PhCN (102.2 Å^2) < $PhNO_2$ (102.4 Å^2), as expected from the solvent sizes. Weak H bonding occurs between the H atoms of the CH_2Cl_2 and the O atoms of the tris(oxalato)metalate(III) anion closest to it (H57−O7, 2.21 Å). The average Cr−O bond length is 1.968 Å, almost identical with that observed in ammonium tris(oxalato)chromate (1.96 Å at 293 K).

The magnetic susceptibility was recorded on a polycrystalline sample cooled to 2 K in a field of 1 T, followed by data collection on warming from 2 to 300 K in the same field. The data were fitted to the Curie−Weiss model with a Curie constant of 1.9 emu K mol^{-1} (1.87 emu K mol^{-1} is expected for spin-only Cr^{3+}) and a Weiss constant of −2.17 K, indicating weak short-range antiferromagnetic interactions between paramagnetic centers. No diamagnetism due to superconductivity was observed at low temperature during zero-field cooled measurements under low applied fields up to 10 G. Magnetization measured at 2 K in applied fields from 0 to 5.5 T fits closely to

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(8) Guionneau, P.; Kepert, C. J.; Chasseau, D.; Truter, M. R.; Day, P. *Synth. Met.* **1997**, *86*, 1973.

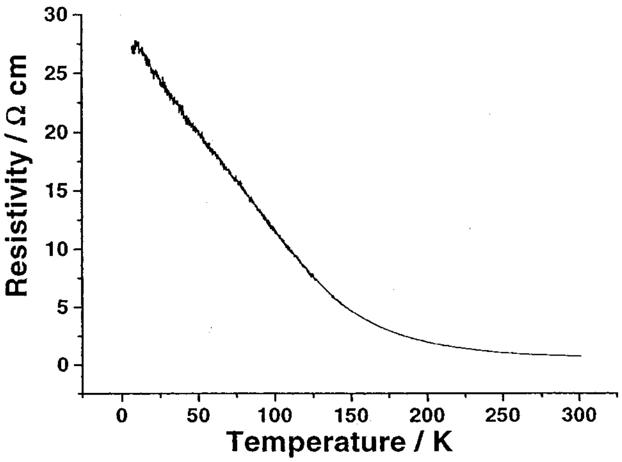

Figure 3. Temperature variation of resistivity for **1**.

a Brillouin function with $S = {}^3/_2$ and $g = 2.0023$. The four-probe conductivity measurements parallel to the *c* axis show that the compound has a room-temperature conductivity of 1.37 S cm^{-1}, which is comparable to that of the superconducting phases, but with an unusual temperature dependence (Figure 3). Close to room temperature the conductivity is almost temperature independent, but below 200 K the resistivity increases with decreasing temperature, although it does not conform to the classical activation behavior of a semiconductor, being nearly linear. The Raman spectrum of a single crystal of **1** contains two broad overlapping bands at 1489(2) and 1468(2) cm^{-1}, arising from the two symmetrical C=C stretching frequencies ν_3 and ν_4. From the previously observed correlation of charge with bond stretching frequency,[9] this corresponds to charges on the two BEDT-TTF molecules of approximately +0.5, in agreement with the bond lengths in the crystal structure. These charges also serve to confirm that the water present within the anion layer must be H_3O^+ in order to maintain overall neutrality.

Conclusions

A further example of a β''-(BEDT-TTF)$_4$[(H$_3$O)M(C$_2$O$_4$)$_3$]S salt has been reported here with S = CH$_2$Cl$_2$, showing that it is not necessary for S to be an aromatic molecule in order to stabilize this type of phase. However, when S is significantly smaller than the volume of the hexagonal cavity between the H_3O^+ and $[M(C_2O_4)_3]^{3-}$ in the honeycomb layer, this leads to some disorder of the terminal $-CH_2CH_2-$ groups of the BEDT-TTF molecules, corresponding to two alternative conformations of the six-membered alicyclic ring. Such disorder has a dramatic effect on the physical properties. All the phases are metallic at room temperature, but when S fills the hexagonal cavity, so that there is no disorder, the phase becomes superconducting at low temperature. In contrast, when disorder is present there is a transition to activated conductivity at low temperature, which may be sharp (S = C$_5$H$_5$N)[6] or broad as in the present case. The role of disorder in opening a gap at the Fermi surface remains to be clarified, as also the extent to which other S molecules can be incorporated in this structure. It is particularly intriguing that disorder among the terminal groups of the BEDT-TTF should have such a large influence on the conductivity, since these electrons do not contribute significantly to the Fermi surface. Furthermore, the fact that different BEDT-TTF $-CH_2$-CH_2- groups become disordered in the S = C$_5$H$_5$N, CH$_2$Cl$_2$ solvates illustrates the complexity of supramolecular chemistry in this class of magnetic molecular metals.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Wang, H. H.; Ferraro, J. R.; Williams, J. M.; Geiser, U.; Schlueter, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 1893.

(10) Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976. Farrugia, I. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.