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Synthesis, crystal structure and properties of the semiconducting molecular charge-transfer salt (bedt-ttf)$_2$Ge(C_2O_4)$_3$·PhCN [bedt-ttf = bis(ethylenedithio)tetrathiafulvalene]

Lee Martin,[a,b] **Scott S. Turner,***[a] **Peter Day,***[a] **Philippe Guionneau,**[c,d]
Judith A. K. Howard,[c] **Mikio Uruichi**[b] **and Kyuya Yakushi**[b]

[a]*Davy-Faraday Research Laboratory, Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS. E-mail: pday@ri.ac.uk, sst@ri.ac.uk*
[b]*Institute of Molecular Science, Myodaichi, Okazaki, 444, Japan*
[c]*Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*
[d]*Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matiére Condensée de Bordeaux, 33608 Pessac Cedex, France*

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The synthesis, crystal structure and physical properties of a new bedt-ttf charge transfer salt containing the tris(oxalato)germanium(IV) anion are described and interpreted. Electrochemical oxidation of neutral bedt-ttf in the presence of $(NH_4)_2Ge(C_2O_4)_3{\cdot}2H_2O$ in PhCN solution yields crystals of (bedt-ttf)$_2$Ge(C_2O_4)$_3$·PhCN. The crystal structure has been solved at 296(2) and at 120(2) K. In contrast to the well known tris(oxalato)-metallate(III) salts of bedt-ttf, the structure does not contain alternating layers of bedt-ttf cations and tris(oxalato)metallate anions, but consists of a 'checker board' arrangement of face-to-face bedt-ttf dimers with $[Ge(C_2O_4)_3]^{2-}$ interspersed by layers of solvent molecules. Each bedt-ttf molecule has a charge close to +1, which is estimated from the empirical relationship between C=C and C–S bond lengths and these charges are correlated with Raman spectra. As expected from the presence of strongly dimerised (bedt-ttf$^+$)$_2$ units the salt is a semiconductor between 300 and 120 K with a low activation energy of 0.127 eV.

Introduction

Molecular charge-transfer salts of the organo-chalcogenide donor bedt-ttf, bis(ethylenedithio)tetrathiafulvalene, are of exceptional interest to solid state chemists and physicists working on low-dimensional narrow-band conductors because of the extraordinary diverse range of electronic ground states that they exhibit.[1,2] Among them are insulators, semiconductors, metals, superconductors, charge and spin density waves and spin-Peierls systems. This variety arises partly from the large number of crystal structures and donor packing motifs that are found, but also from the extreme sensitivity of the collective electronic properties to small changes in inter-donor distances and orientations which are generally driven by the packing requirements of the anions. The tris(oxalato)metallate(III) family of salts with bedt-ttf illustrates this complexity nicely. In the past few years they have been of particular significance because they have furnished the first examples of paramagnetic molecular superconductors, which are the first superconductors of any kind to contain paramagnetic moments originating from 3d orbitals.[3–6] Furthermore this family contains examples of semiconducting[4] materials and even one which displays a metal–insulator transition.[7] The transport characteristics can be related to structural changes and/or small changes to the constituents of the salt.

The crystal structures of a number of materials with the general formula (bedt-ttf)$_4$A^{I}M^{III}(C_2O_4)$_3$·solvent, where A is a monovalent cation such as K^+, H_3O^+ or $NH_4{}^+$, have been solved. Changes have been possible not only to A and the metal ion, M, but also to the solvent molecule.[7,8] Structurally they consist of alternating layers containing bedt-ttf cations and approximately hexagonal arrangements of the $[M(C_2O_4)_3]^{3-}$ anion and A, in which the latter are inserted into six-coordinate cavities formed from the uncoordinated O atoms in the C_2O_4 ligands.[4,9] This arrangement of tris(oxalato)metallate(III) ions is quite widespread and has been found in a large class of molecule based magnets.[10] It is therefore of interest to prepare bedt-ttf phases in which the charge on the tris(oxalate) anion is not −3, which would induce a different anion and subsequently cation packing sequence. In particular, if the anion charge were −2, the monovalent cation, A, would not be required to ensure overall charge neutrality, assuming that the bedt-ttf : anion stoichiometry is retained as in the M(III) materials. For this reason we have prepared a bedt-ttf charge transfer salt with the tris(oxalato)germanate(IV) anion, and here, we report its synthesis, structure and properties.

Experimental

Synthesis and purification of starting materials

$(NH_4)_2Ge(C_2O_4)_3{\cdot}H_2O$ was synthesised by refluxing an aqueous solution (75 ml) containing germanium oxide (1.57 g, 15 mmol), ammonium oxalate monohydrate (1.83 g, 12.8 mmol) and oxalic acid (4.04 g, 44.6 mmol) until all the solids had dissolved.[11] Upon cooling to 40 °C, 90% ethanol (80 ml) was added and the product was precipitated on further cooling. The solid was washed with ice cold water–ethanol (50 : 50, v/v). The crude product recrystallised from a hot mixture of H_2O (30 ml) and 95% ethanol (30 ml). Large white crystals formed, which were washed with ice-cold ethanol (25 ml) followed by ice-cold diethyl ether (25 ml) and dried under vacuum. Yield = 4.1 g (60%). Elemental analysis. Calc. (found) for $(NH_4)_2Ge(C_2O_4)_3{\cdot}H_2O$: C 18.44(18.52), H 2.58(3.13), N 7.17(7.45)%.

Bedt-ttf (Aldrich) was recrystallised twice from chloroform, 18-crown-6 (Aldrich) was dried over acetonitrile and benzonitrile (Aldrich) was fractionally distilled at low pressure over P_2O_5 immediately prior to use.

Electrocrystallisation

Three-compartment H-shaped cells with approximate volume of 50 ml were used for crystal growth of the title compound by electrocrystallisation. Each cell had two Pt electrodes, separated by two porous glass frits to prevent contamination by reduction products. Prior to use, the H-cells were washed with *aqua regia* followed by distilled H_2O, and were then dried thoroughly. The Pt electrodes were cleaned by washing in conc. HNO_3 followed by applying 9 V across the electrodes dipped in 1 M H_2SO_4 for 5 min in each direction, giving evolution of H_2 and O_2. Finally the electrodes were washed in distilled water followed by methanol and then were thoroughly dried. During crystal growth the H-cell joints were sealed to prevent solvent evaporation.

The electrocrystallisation method involves the *in situ* anodic oxidation of a neutral organic donor molecule (in this case bedt-ttf) in a solution containing a salt of the anion to be incorporated into the charge-transfer salt. The anion in solution also serves as the supporting electrolyte. A constant current source was used to control the crystal growth rate. The cells were fixed inside sand-filled compartments on a concrete table, to minimise vibration and were kept at a constant temperature of 295(2) K.

100 mg $(NH_4)_2Ge(C_2O_4)_3 \cdot H_2O$ and 200 mg 18-crown-6 were suspended in 50 ml of freshly distilled benzonitrile. One drop of water was added and the mixture stirred until all solids had dissolved. 10 mg of bedt-ttf was placed in the base of the anode side of the H-shaped cell and the remainder was filled with the filtered benzonitrile solution. A current of 1 μA was passed across the cell and crystals grew on the anode slowly over 21 days. A large quantity of well formed black needles of (bedt-ttf)$_2$Ge$(C_2O_4)_3 \cdot$PhCN were obtained (average size 0.40 × 0.10 × 0.10 mm) and were found to be suitable for X-ray structure determination.

Physical measurements

Two-probe DC transport measurements were made on several crystals of the title compound and since they had high intrinsic resistances the contact resistances were assumed to be negligible. Gold wire electrodes (0.025 mm diameter) were attached directly to the crystals using Pt paint (Degussa) and the attached wires were connected to a standard eight-pin integrated circuit plug with Ag paint (RS components). Ag paint was not used for contacts direct onto the sample owing to the possible formation of the insulator AgS at the electrode–crystal interface. The eight-pin plugs were mounted onto a copper block in an Oxford instruments CF200 continuous-flow cryostat and variable temperature resistance measurements taken with a Hewlett-Packard 3478A digital multimeter.

Polarised IR reflectance spectra were measured using a Spectra-Tech IR-plan microscope fitted in the light path of the sample chamber of a FT-IR Nicolet Magna 760 spectrometer. Spectra were collected between 600 and 4000 cm^{-1} using an IR light source, MCT detector, KBr beam splitter and wire grid polariser with 4 cm^{-1} resolution; between 3500 and 10 000 cm^{-1} using a white light source, MCT detector, quartz beam splitter and NIR/VIS Glan-Thompson polariser with 32 cm^{-1} resolution. The absolute reflectivity was obtained by comparison with the reflected light from a gold mirror placed close to the sample. Spectra from 10 000 to 32 000 cm^{-1} were measured using the same microscope set up, combined with a multi-channel detection system (Atago Macs320) using a xenon lamplight source with a Glan-Thompson prism polariser.

Raman spectra of single crystals were measured at room temperature on a Renishaw Raman imaging microscope using a He–Ne laser (632.6 nm) with a 10% filter. Samples were measured both parallel and perpendicular to the incident beam from 100 to 4000 cm^{-1} whilst higher resolution scans were performed from 1150 to 1650 cm^{-1} to observe the bedt-ttf ν_3 and ν_4 frequencies (see below). Spectra were identical when measured both parallel and perpendicular to the incident beam with negligible changes in peak positions.

Structure determination

The crystallographic study was performed using a Bruker SMART-CCD diffractometer with Mo-Kα radiation and an Oxford Cryosystem N_2 open flow cryostat. The crystals are very fragile black needles and preliminary X-ray diffraction images showed poor quality diffraction patterns owing to twinning but one crystal was good enough to collect data and was used for both ambient temperature (296 K) and low temperature (120 K) experiments. At 296 K, the full set of data was collected based on four ω-scans runs (starting $\omega = -26$, -21, -23, $-26°$, respectively) at values $\phi = 0$, 88, 180, 0° with the detector at $2\theta = -29°$ for the three first runs and $+29°$ for the last one. At each of these runs, frames (606, 435, 606, 100 respectively) were collected at 0.3° intervals and at 20 s per frame. At 120 K, the full data set was collected based on four ω-scans (starting $\omega = 26$, -21, -26, $-21°$, respectively) at values $\phi = 0$, 88, 180, 268° with the detector fixed at $2\theta = -29°$. At each of these runs, frames (909, 653, 909, 100, respectively) were collected at 0.2° intervals and 15 s per frame. These strategies both correspond to θ values lower than 28° with completeness for this θ range being $>99.7\%$. The diffraction frames were integrated using the SAINT package[12] and corrected with SADABS.[13] The crystal structures were solved with the SHELXTL-plus programs.[14] Among this series of salts, it is quite common to find structural disorder on the bedt-ttf molecule extremities. In the present case, it is the anionic part that presents a very strong disorder. We could not adequately resolve such disorder at room temperature and so we completed a low temperature experiment, together with changing some of the data collection parameters. The disorder is reduced at 120 K, which indicates its dynamic origin, though it remains strong and is responsible for the relatively high values of the structural quality criteria. Thus, residual peaks (1.8 e $Å^{-3}$) are present close to the oxalate and the Ge ion but no significant peaks can be seen outside the anion and we assume the packing of the bedt-ttf, discussed later, is not affected. We also note that the solvent, PhCN, is not affected by disorder in contrast to a number of the (bedt-ttf)$_4$M-(oxalate)$_3$·solvent series.[4,15]

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/179. See http://www.rsc.org/suppdata/jm/1999/2731/ for crystallographic files in .cif format.

Description of crystal structure at 296 and 120 K

The charge carried by the anion is an important factor in determining the charge distribution and packing motif of the bedt-ttf molecules, and the overall stoichiometry in this class of charge-transfer salt. In the present case the charge associated with the tris(oxalato)germanate(IV) anion is 2− [compared to 3− for the $M^{III}(C_2O_4)_3$ anions] and this leads to the formation of a unique bedt-ttf packing arrangement in (bedt-ttf)$_2$Ge$(C_2O_4)_3 \cdot$PhCN. As expected, in contrast to tris(oxalato)metallate(III) salts, it contains no H_3O^+ or NH_4^+, although the ratio of bedt-ttf to M is 2 : 1 not 4 : 1. Table 1 lists the crystallographic data and Fig. 1 shows standard ORTEP diagrams at both experimental temperatures, with the H atoms omitted for clarity. The anion disorder at 296 K can clearly be seen from the 50% thermal ellipsoids in Fig. 1(a).

Table 1 Crystallographic data for (bedt-ttf)$_2$[Ge(C$_2$O$_4$)$_3$]·PhCN at 296 and 120 K^a

T/K	296(2)	120(2)
Chemical formula	$C_{33}H_{21}NO_{12}S_{16}Ge$	$C_{33}H_{21}NO_{12}S_{16}Ge$
M	1209.06	1209.06
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	18.733(1)	18.454(1)
b/Å	11.066(1)	10.993(1)
c/Å	23.058(1)	23.080(1)
β/°	112.5(1)	112.4(1)
V/Å^3	4416(1)	4328(1)
Z	4	4
μ/mm^{-1}	1.51	1.54
Measured reflections	37 525	35 583
Independent reflections	10 047	9892
R_{int} (%)	15.5	8.2
R	0.107	0.077
$wR(F^2)$	0.23	0.18

^{a} Note: the anion is strongly disordered.

There are no discrete anionic and cationic layers in this compound. Instead the bedt-ttf molecules form dimers separated by single tris(oxalato)germanate(IV) anions in the a and c directions, and by a single tris(oxalato)germanate(IV) anion and a layer of benzonitrile molecules along the b axis. For the structure at 120 K Fig. 2(a) shows a crystal packing diagram along the b direction showing molecular overlap; Fig. 2(b), in the c direction, shows a space filling diagram which better illustrates the 'checker board' packing pattern.

At 296 K (bedt-ttf)$_2$Ge(C$_2$O$_4$)$_3$·PhCN has two independent bedt-ttf molecules. The molecule with central bond C(15)=C(17) has a 'boat' conformation at one end and a 'twisted' conformation at the other whereas the other donor molecule has a 'boat' conformation at both ends. The 'boat' conformation is defined here when both ethylene carbon atoms are on the same side of the central ttf plane and the 'twisted' conformation has one carbon atom of the ethylene unit on either side of the plane. The 'boat–boat' molecule is bent from planarity at both ends probably as a result of steric interaction with the oxalate ligands in the anion, an effect which is increased at 120 K. There are three short face-to-face S···S contacts (below the van der Waals distance of 3.6 Å) between the two crystallographically independent bedt-ttf molecules of each dimer pair; S(8)–S(14) is 3.54(1) Å at 296 K equivalent to S(3)–S(12) which is 3.50(1) Å at 120 K; S(7)–S(13) is 3.53(1) Å at 296 K equivalent to S(11)–S(4) which is 3.47(1) Å at 120 K;

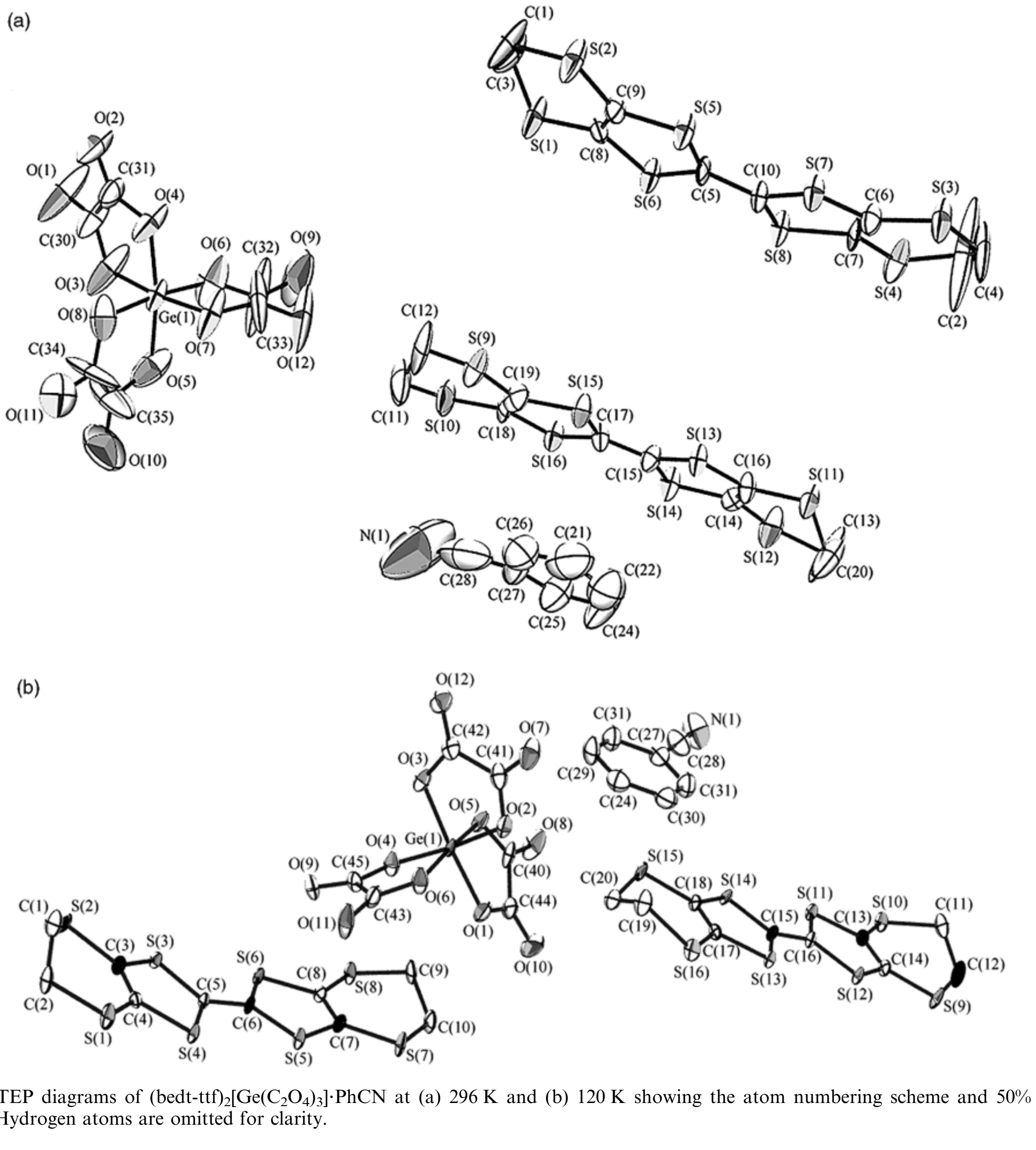

Fig. 1 ORTEP diagrams of (bedt-ttf)$_2$[Ge(C$_2$O$_4$)$_3$]·PhCN at (a) 296 K and (b) 120 K showing the atom numbering scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

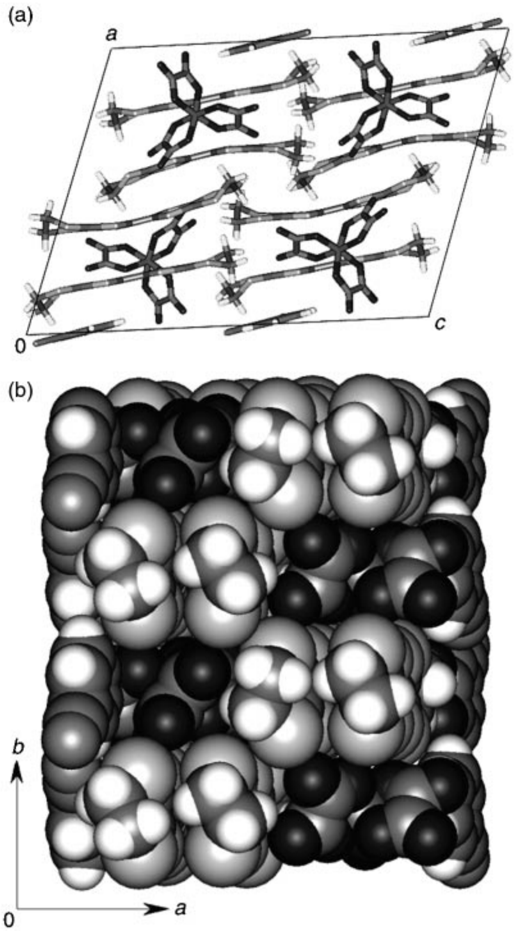

Fig. 2 (a) Packing diagram of (bedt-ttf)$_2$[Ge(C$_2$O$_4$)$_3$]·PhCN viewing along the *b* direction and (b) space filling projection along the *c* axis.

S(6)–S(16) is 3.51(1) Å at 296 K equivalent to S(6)–S(13) which is 3.49(1) Å at 120 K. There are also two side-to-side close contacts between S atoms in the outer six-membered rings of crystallographically equivalent molecules in neighbouring dimers; S(1)–S(4) is 3.48(1) Å at 296 K equivalent to S(10)–S(15) which is 3.38(1) Å at 120 K; S(2)–S(3) is 3.63(1) Å at 296 K equivalent to S(2)–S(8) which is 3.45 Å at 120 K. See Fig. 1 for the relevant numbering scheme at each temperature.

The arrangement of the [Ge(C$_2$O$_4$)$_3$]$^{2-}$ anions as shown in Fig. 2 shows that they form layers parallel to the {100} plane, which are built up of rows which have alternating Δ and Λ enantiomers. Within a given row of Ge(C$_2$O$_4$)$_3$$^{2-}$ enantiomers, adjacent molecules are transposed by 180°. Selected bond lengths and angles within the [Ge(C$_2$O$_4$)$_3$]$^{2-}$ anion are listed in Table 2 with the atom-numbering scheme shown in Fig. 1. By comparison with other oxalato complexes, the C–C bonds of the ligands are significantly shorter than expected at room temperature [1.33(2) and 1.40(2) Å × 2], an anomaly that is absent at 120 K [1.51(2), 1.52(2) and 1.53(2) Å]. This anomaly at room temperature is due to the strong thermal disorder, which affects the anionic part at high temperature and is reduced at 120 K.

Table 2 Selected bond lengths (Å) for the [Ge(C$_2$O$_4$)$_3$]$^{2-}$ anion

120 K		296 K	
Ge(1)–O(1)	1.877(6)	Ge(1)–O(3)	1.879(9)
Ge(1)–O(2)	1.879(6)	Ge(1)–O(4)	1.841(8)
Ge(1)–O(3)	1.883(5)	Ge(1)–O(5)	1.847(10)
Ge(1)–O(4)	1.888(6)	Ge(1)–O(6)	1.880(9)
Ge(1)–O(5)	1.876(5)	Ge(1)–O(7)	1.842(8)
Ge(1)–O(6)	1.887(6)	Ge(1)–O(8)	1.900(16)

The spatial organisation of the tris(oxalato)germanate(IV) anions results in numerous short atomic contacts between the oxygen atoms and the terminal ethylene hydrogen atoms of the donor molecules. In particular the contact O(1)···H(1B) [bonded to C(1)] increased markedly upon cooling from 296 K [2.93(3) Å] to 120 K [3.73(2) Å], as a consequence of increased deviation from planarity at both ends of the 'boat–boat' bedt-ttf molecule.

The benzonitrile molecules are arranged in layers parallel to the {001} plane, with the benzene rings tilted slightly out of this plane, and the C≡N bonds pointing alternately above and below the plane. It is noteworthy that the C≡N bond is significantly longer at 296 K [1.339(4) Å] than at 120 K [1.202(13) Å], and furthermore the C–C≡N angle at 296 K [179.0(1)°] is larger than at 120 K [171.5(3)°].

The estimation of charge associated with each bedt-ttf donor molecules in charge-transfer salts is an important aid to understanding the physical properties of these salts. More than one crystallographically independent bedt-ttf molecule is found in many charge-transfer salts with the possibility of charge localisation. Theoretical calculations on the bedt-ttf molecule in various oxidation states indicate it is the central region of the bedt-ttf molecule which donates charge upon oxidation, and also undergoes the largest changes to bond lengths. The charges on the bedt-ttf cations have been estimated by direct experimental observation of the length of the central C=C bond.[16] More recently, through a systematic search of the Cambridge Structural Database of all high-quality bedt-ttf structures, its charge has been compared with bond lengths in the central ttf portion of the molecule.[17] Oxidation of bedt-ttf has the effect of lengthening the C=C bonds that are bonding with respect to the HOMO and shortening the C–S bonds, which are antibonding with respect to the HOMO. There are also smaller changes to the bond lengths in the outer six-membered rings of the molecule, but structural disorder and increased thermal vibration have prevented any systematic observation. The study by Guionneau and Kepert *et al.*[17] showed that the charge, Q, on a bedt-ttf molecule can be estimated quite precisely from an empirically determined relationship between the C=C and C–S bonds and Q. This relationship was shown to provide an estimation of the charge with approximately twice the precision of earlier methods, which took into account only the central C=C bond. With the standard deviation in bond lengths and the few examples for bedt-ttf and bedt-ttf^{2+}, the accuracy in the charge estimation of this model was reported as close to 10%. Based on these considerations, the germanium salt shows values of Q close to $+1$ (actual values are 1.1, 1.2 at 120 K and 1.1, 1.3 at 296 K), as expected for (bedt-ttf)$_2$$^{2+}$Ge^{4+}(C$_2O_4$)$_3$$^{6-}$·PhCN, though at both 296 and 120 K the 'boat–twisted' bedt-ttf molecule has a slightly higher charge than the other.

Results of physical measurements

Two-probe transport measurements parallel to the needle axis were performed from ambient temperature to 120 K recording the resistance, R, every 0.5 K at 1 K min^{-1}. A plot of ln R *vs.* 1000/T gives a straight line from which a linear fit gives an activation energy of 0.127 eV, confirming that the title compound is a semiconductor, with a modest band gap along the needle axis.

The Raman spectrum of (bedt-ttf)$_2$Ge(C$_2$O$_4$)$_3$·PhCN is shown in Fig. 3(a) and (b). The two totally symmetrical C=C stretching frequencies $\nu_3 = 1459/1445$ cm^{-1} and $\nu_4 = 1410/1406$ cm^{-1} [Fig. 3(b)] correspond to charges of $+1.0/+1.1$ with equal weighting given to each peak using the equations of Wang *et al.*[18] Further Raman active peaks of the bedt-ttf molecules are observed in the spectrum: $\nu_5 = 1282$ cm^{-1},

Table 3 Selected bond lengths (Å) for bedt-ttf molecules used in charge estimation

296 K	'Boat–boat'		'Boat–twisted'
C(5)–C(10)	1.404(12)	C(15)–C(17)	1.406(13)
C(5)–S(6)	1.709(10)	C(15)–S(14)	1.696(11)
C(5)–S(5)	1.710(11)	C(15)–S(13)	1.724(11)
C(10)–S(8)	1.703(11)	C(17)–S(15)	1.712(11)
C(10)–S(7)	1.740(10)	C(17)–S(16)	1.718(11)
S(8)–C(7)	1.758(10)	S(14)–C(14)	1.744(12)
S(5)–C(9)	1.697(10)	S(13)–C(16)	1.721(11)
S(6)–C(8)	1.751(10)	S(16)–C(18)	1.737(11)
S(7)–C(6)	1.762(11)	S(15)–C(19)	1.737(12)
C(6)–C(7)	1.332(13)	C(19)–C(18)	1.369(15)
C(8)–C(9)	1.368(13)	C(16)–C(14)	1.364(14)
120 K	'Boat–boat'		'Boat–twisted'
C(5)–C(6)	1.409(9)	C(15)–C(16)	1.409(9)
C(5)–S(3)	1.738(7)	C(15)–S(13)	1.717(7)
C(5)–S(4)	1.724(7)	C(15)–S(14)	1.723(7)
C(6)–S(5)	1.709(7)	C(16)–S(11)	1.725(7)
C(6)–S(6)	1.722(7)	C(16)–S(12)	1.717(7)
S(3)–C(3)	1.751(7)	S(13)–C(17)	1.750(7)
S(4)–C(4)	1.750(7)	S(14)–C(18)	1.746(7)
S(5)–C(7)	1.744(7)	S(12)–C(14)	1.741(7)
S(6)–C(8)	1.740(7)	S(11)–C(13)	1.738(7)
C(3)–C(4)	1.359(10)	C(13)–C(14)	1.375(11)
C(7)–C(8)	1.370(10)	C(18)–C(17)	1.365(11)

$\nu_6 = 1002\ \mathrm{cm}^{-1}$, $\nu_7 = 899\ \mathrm{cm}^{-1}$, $\nu_8 = 648\ \mathrm{cm}^{-1}$, $\nu_9 = 511/497\ \mathrm{cm}^{-1}$, $\nu_{10} = 478/453\ \mathrm{cm}^{-1}$ and $\nu_{11} = 304\ \mathrm{cm}^{-1}$.

The polarised IR reflectivity measured with the electric vector both parallel and perpendicular to the needle axis of a crystal show a low reflectivity characteristic of a semiconductor with sharp vibrational features superimposed [Fig. 4(a) and (b)]. Several of the peaks in the perpendicular polarised direction can be assigned to the $[\mathrm{Ge(C_2O_4)_3}]^{2-}$ ion: O–C–O stretching vibrations at 1275 and 1319 cm^{-1}, an O–C–O symmetric stretching vibration at 1396 cm^{-1} and an O–C–O asymmetric vibration at 1716–1734 cm^{-1} [Fig. 4(b)]. The reflectivity intensity in the near-IR and visible regions [Fig. 4(a)] is much higher in the perpendicular direction. This implies that conductivity would be increased perpendicular to the crystal needle axis compared to that measured parallel to this axis. The size and shape of the crystal prevented direct transport measurements in this direction.

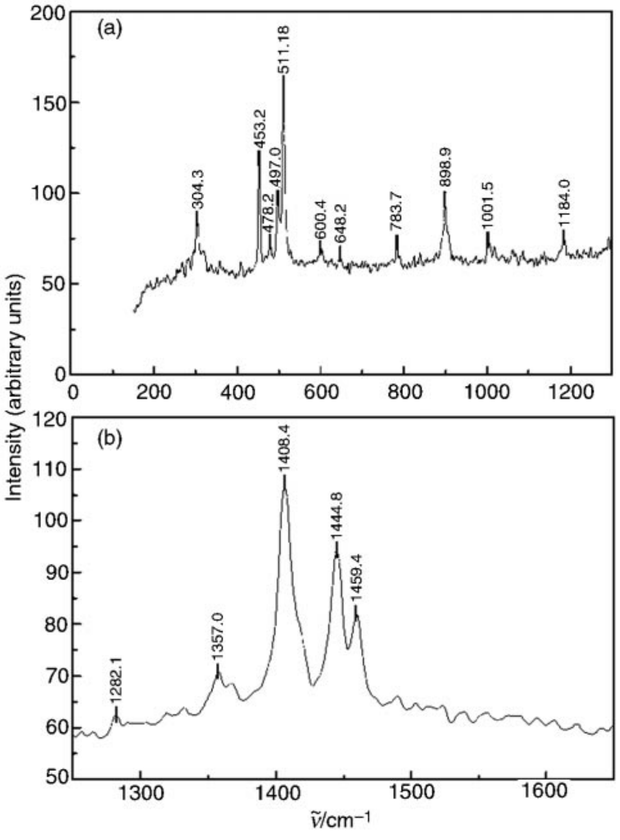

Fig. 3 Raman spectra of (bedt-ttf)$_2$[Ge(C$_2$O$_4$)$_3$]·PhCN: (a) 200–1300 cm^{-1} and (b) 1250–1650 cm^{-1}.

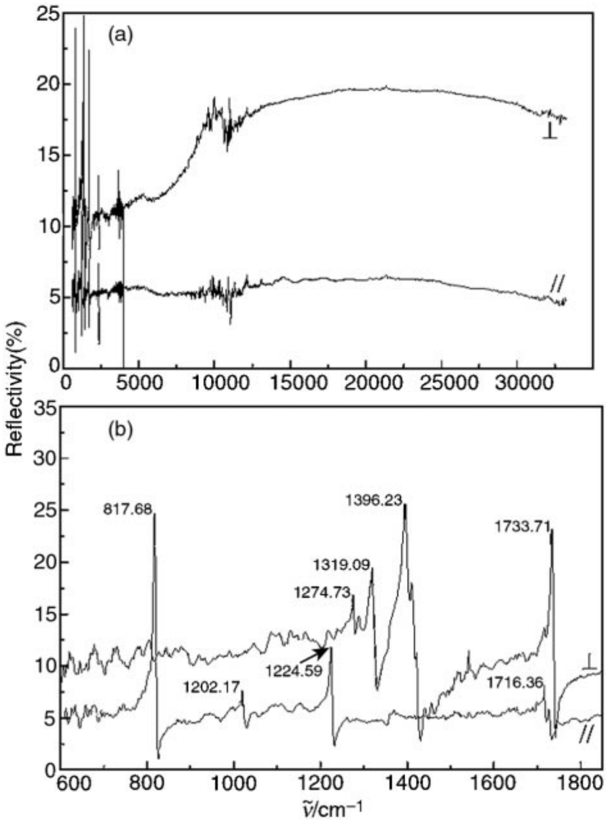

Fig. 4 Polarised IR reflectivity spectra of (bedt-ttf)$_2$[Ge(C$_2$O$_4$)$_3$]·PhCN: (a) 600–35 000 cm^{-1} and (b) 600–1825 cm^{-1}.

Conclusion

We have shown that it is possible to change the charge on the tris(oxalato)metallate anion from −3 to −2, in a similar synthesis method used for preparation of bedt-ttf charge transfer salts with general formula (bedt-ttf)$_4$AM(C$_2$O$_4$)$_3$·PhCN. This is done by replacing a 3d metal, M, such as Cr(III) or Fe(III) with Ge(IV) and has the effect of removing A from the lattice which destabilises the hexagonal AM(C$_2$O$_4$)$_3$ layer. The new salt (bedt-ttf)$_2$Ge(C$_2$O$_4$)$_3$·PhCN consists of a 'checker board' arrangement in which discrete face-to-face bedt-ttf dimers alternate with $[\mathrm{Ge(C_2O_4)_3}]^{2-}$ in three dimensions. The bond lengths of the donor cations indicate that the dimers carry a charge of +2, a conclusion reinforced by the Raman active C=C stretching frequencies. In agreement with strong electron pairing in the (bedt-ttf^{+})$_2$ unit the salt is a semiconductor.

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