Novel silver(I) complexes derived from tetrakis(methylthio)-tetrathiafulvalene and bis(ethylenedithio)tetrathiafulvalene with 3D and 1D structures

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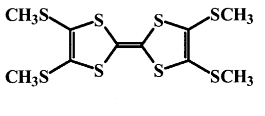
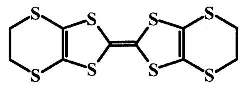
Novel silver(I) complexes **1** and **2** derived from tetrakis(methylthio)tetrathiafulvalene (TMTTTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), respectively, were prepared by the self-assembly approach. Their crystal structures were determined. Complex **1** shows a three-dimensional structure with an unprecedented 4.16-net porous inorganic layer of silver nitrate. In complex **2**, silver(I) is coordinated to the BEDT-TTF$^+$ cation and an extended 1D "zig-zag" chain is formed. The electrical conducting properties of complex **1** (after oxidation by iodine) and complex **2** were investigated.

In recent years, various silver(I) complexes with interesting and sophisticated structures have been prepared and characterized.[1] For instance, Hong *et al.*[1g] reported a silver(I) coordination polymer chain containing nanosized tubes. In some coordination polymers[2] the ligands are organic functional molecules that may induce the resulting molecular assembly systems to display interesting physical properties such as electrical conductivity. Tetrathiafulvalene (TTF) and its derivatives have been extensively studied as electron donors for organic conductors and superconductors.[3] The sulfur atoms in TTF derivatives such as tetrakis(methylthio)tetrathiafulvalene (TMTTTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) might form coordination bonds with silver ions to generate metallic complexes with interesting structures. These complexes may also display conducting properties after suitable oxidation. Moreover, the intermolecular arrangements of electron donors obtained in such kinds of complexes may not be easily accessible by conventional electrochemical and diffusion methods, and hence may provide unique examples for the studies of structure-property relations.



TMTTTF



BEDT-TTF

Munakata *et al.*[4] once described the copper(I) complexes of TMTTTF, tetrakis(ethylthio)tetrathiafulvalene and tetrakis(propylthio)tetrathiafulvalene with one- or two-dimensional structures. Inoue *et al.*[5] observed the coordination of the BEDT-TTF$^+$ cation to copper(I) ion. In this paper, we wish to report two new silver(I) complexes, one with TMTTTF (complex **1**) exhibiting a novel 3D structure with a 4.16-net porous inorganic layer of silver nitrate, and the other with BEDT-TTF (complex **2**) forming an extended 1D "zig-zag" chain, in which silver(I) is coordinated to BEDT-TTF$^+$ cations. In addition, we will also report the electrical conducting properties of complex **1** (after oxidation) and complex **2**.

Experimental

General

The FT-IR spectra were recorded on a Pekin–Elmer 2000 in the form of KBr platelets. The elemental analysis data were obtained with a Heraeus CHN-Rapid. XPS data were obtained with a VG Scientific Escalab 220I-XL. The electrical conductivity was measured using the conventional four-probe method.

X-Ray crystallography

The intensity data were collected on a Bruker SMART APZX CCD area detector with a graphite monochromator for the Mo-Kα ($\lambda = 0.71073$ Å) radiation at 293 K. The diffraction data were corrected with an empirical method (SADABS[6]). The structure was solved by direct methods with the SHELXS97[7] program, and refined with full-matrix least-squares methods. Non-hydrogen atoms except for the oxygen and nitrogen atoms of nitrate groups in complex **2** were refined anisotropically. The oxygen and nitrogen atoms of nitrate groups in complex **2** are highly disordered[8] and they were treated isotropically. Hydrogen atoms were theoretically added and included in the final refinement. The crystallographic and refinement data are summarized in Table 1. Selected bond lengths and angles of these two complexes are listed in Table 2.

CCDC reference numbers 166350 and 180255. See http// www.rsc.org/suppdata/ nj/b1/b108823h/ for crystallographic data in CIF or other electronic format.

Syntheses

Complex 1. A solution of TMTTTF (10 mg, 0.026 mmol) dissolved in 10 ml of DMF in a glass tube was layered with 3 ml of anhydrous methanol. To the top layer of the above system 10 ml of saturated AgNO$_3$ dissolved in methanol was carefully added, and the glass tube was left in a dark place at room temperature. After 10 days, red crystals of complex **1**

Table 1 Crystallographic and refinement data of complexes **1** and **2**

	1	**2**
Chemical formula	$C_5H_6AgNO_3S_4$	$C_{10}H_8AgN_2O_6S_8$
Formula weight	364.22	616.53
T/K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	Cc
a/Å	14.240(3)	27.637(6)
b/Å	9.1260(18)	4.2730(9)
c/Å	8.1013(16)	18.839(4)
α/°	90	90
β/°	92.93(3)	125.52(3)
γ/°	90	90
U/Å^3	1051.5(4)	1810.7(6)
Z	4	4
μ/mm^{-1}	2.688	2.070
Reflns collected	9769	7911
Reflns unique	3893	4508
Reflns observed	2545	1614
$R_1{}^a$ $[I \geqslant 2\sigma(I)]$	0.0367	0.0490
$wR_2{}^b$ $[I \geqslant 2\sigma(I)]$	0.0734	0.0716

^{a} $R_1 = \dfrac{\sum[|F_o| - |F_c|]}{\sum|F_o|}$. ^{b} $wR_2 = \left\{\dfrac{\sum[w(F_o{}^2 - F_c{}^2)]}{\sum[w(F_o{}^2)]}\right\}^{1/2}$

were obtained: yield (5 mg, 27%), Anal. found (calcd) for $C_5H_6AgNO_3S_4$: C 16.31 (16.49), H 1.42 (1.66), N 3.78 (3.85). IR (KBr): 1413.6 (s), 1383.9 (vs), 1300.6 (s) cm^{-1}.

Complex 2. A solution of 20 mg (0.052 mmol) of BEDT-TTF in 10 ml of dichloromethane was added to one side of an H-tube. To the another side of the H-tube 10 ml of a saturated solution of silver nitrate in methanol was added. Then, methanol was carefully added to both sides of the H-tube until the two sides were bridged. After the H-tube was left in the dark for 10 days at room temperature, black crystals of complex **2** were obtained (8 mg, yield 25%), among which suitable crystals were selected for crystal structural analysis and electrical conductivity measurement. Anal. found (calcd) for $C_{10}H_8AgN_2O_6S_8$: C 19.19 (19.48), H 1.56 (1.31), N 4.28 (4.54). IR (KBr): 1383.4, 1276.6, 1233.2, 1158.0, 1124.8 cm^{-1}.

Table 2 Selected bond lengths (Å) and angles (°) of complexes **1** and **2**

Complex **1**		Complex **2**	
S(1)–C(4)	1.748(3)	Ag(1)–O(21)	2.4593(16)
S(1)–C(1)	1.803(3)	Ag(1)–O(11)	2.5253(19)
S(2)–C(3)	1.746(2)	Ag(1)–S(1)^{iv}	2.6917(11)
S(2)–C(2)	1.808(3)	Ag(1)–S(7)	2.7295(10)
S(3)–C(4)	1.754(3)	S(3)–C(3)	1.7046(17)
S(3)–C(5)	1.762(3)	S(3)–C(5)	1.708(2)
S(4)–C(5)	1.755(3)	S(4)–C(5)	1.652(2)
S(4)–C(3)	1.756(2)	S(4)–C(4)	1.717(2)
C(3)–C(4)	1.355(4)	S(5)–C(8)	1.7660(18)
C(5)–C(5A)^{i}	1.334(5)	S(5)–C(6)	1.769(3)
Ag(1)–S(1)	2.6476(10)	S(6)–C(7)	1.730(2)
Ag(1)–S(2)	2.6772(9)	S(6)–C(6)	1.757(2)
Ag(1)–O(2)	2.570(2)	C(1)–C(2)	1.565(4)
Ag(1)–O(3A)^{ii}	2.4305(19)	C(3)–C(4)	1.393(3)
Ag(1)–O(3B)^{iii}	2.4875(19)	C(5)–C(6)	1.383(2)
S(3)–C(5)–S(4)	113.41(15)	C(7)–C(8)	1.346(3)
S(1)–Ag(1)–S(2)	79.05(3)	C(9)–C(10)	1.407(4)
S(1)–Ag(1)–O(2)	126.29(5)	O(21)–Ag(1)–O(11)	87.90(6)
S(2)–Ag(1)–O(2)	119.03(5)	O(21)–Ag(1)–S(1)^{iv}	95.22(5)
S(1)–Ag(1)–O(3A)	106.03(5)	O(11)–Ag(1)–S(1)^{iv}	114.99(6)
S(2)–Ag(1)–O(3B)	94.86(5)	O(21)–Ag(1)–S(7)	116.63(6)
		O(11)–Ag(1)–S(7)	103.19(6)
		S(1)^{i}–Ag(1)–S(7)	130.90(2)
		S(4)–C(5)–S(3)	121.75(10)
		S(6)–C(6)–S(5)	109.54(9)

Symmetry operators: ^{i} $-x+1, -y+1, -z$; ^{ii} $x, -y+1/2, z+1/2$; ^{iii} $-x, y+1/2, -z+1/2$; ^{iv} $x-1/2, -y+1/2, z-1/2$

Iodine-doped complex 1. The red crystals of complex **1** and solid iodine were separately placed in the left and right sides of an H-tube. Then, the H-tube was sealed and left at ambient temperature for 4 days to partially oxidize complex **1** by iodine vapor. The resulted black I_2-doped complex was subjected to elemental analysis: C, 13.58%; H, 1.20%; N, 3.10%. Based on the elemental analysis, the composition of the doped complex was estimated to be $[C_{10}H_{12}Ag_2N_2O_6S_8]\cdot I_{1.1}$. FT-IR (KBr): 1398.6 (vs) 1335.0 (w), 1314.2 (w), 1107.5 (vs) cm^{-1}.

Results and discussion

Structures of complexes 1 and 2

Complex 1. Fig. 1 shows the structure of one TMTTTF unit coordinated to two silver(I) ions in complex **1**. On the periphery of the silver ion [Ag(1)], there are three oxygen atoms [O(2), O(3A) and O(3B)] and two sulfur atoms [S(1) and S(2)]. Based on their bond lengths and angles, these atoms form a distorted square pyramidal geometry around the silver ion, in which atoms O(3A), O(3B), S(1), and S(2) define the basal plane and atom O(2) occupies the apical position. Atom Ag(1) deviates out of the basal plane by about 0.38 Å. The plane of Ag(1), S(1) and S(2) forms a dihedral angle of 30.3° with the central TTF core in complex **1**. The bond length of the central C=C [C(5)–C(5A)] bond of the TMTTTF unit in complex **1** is 1.334(5) Å. As compared to that of neutral TMTTTF [1.348 (5) Å],[9] it can be inferred that the TMTTTF unit in complex **1** is essentially neutral according to the correlation between the oxidation states of TTF derivatives and the bond lengths of the central C=C bonds.[9] This is fully consistent with the result of the IR measurements. The central C=C stretching frequency of the TMTTTF unit in complex **1** was found to occur at 1413 cm^{-1}, very close to that in free TMTTTF (1410 cm^{-1}).[4b]

In contrast to oxygen atoms O(1), O(1A), O(1B) and O(2), the oxygen atoms O(2A), O(2B), O(3), O(3A) and O(3B) of the crystallographically asymmetric unit shown in Fig. 1 form further coordination bonds with other silver ions, in which O(3), O(3A) and O(3B) are coordinated in the μ_2 mode. Each silver(I) is coordinated by three oxygen atoms from three different nitrate ions. In this way the structure is extended to form an infinite inorganic layer composed of silver and nitrate ions, as indicated in Fig. 2. More interestingly, small tetraatomic rings (Ag_2O_2) and large rings containing 16 atoms (N, O and Ag) alternate in this novel inorganic layer of silver nitrate. It should be mentioned that this is the first inorganic layer containing only silver(I) and nitrate ions with such a 4.16-net porous structure.

The nearest neighboring inorganic layers are linked by TMTTTF molecules through the coordination of methylthio groups to silver ions, and consequently a three-dimensional framework is generated as manifested in Fig. 3. The arrangement of the TMTTTF molecules is also displayed in Fig. 3. The core planes (TTF units) of neighboring TMTTTF molecules are not coplanar and they form a dihedral angle of 55.7°. However, a given TMTTTF molecule is parallel to its next neighbor, and TMTTTF molecules are so alternatingly arranged to produce a column-like structure along the *b* axis. There are no short S–S contacts among the neighboring TMTTTF molecules but there are short S–Ag contacts (4.05 Å).

Complex 2. Complex **2** is formulated as [BEDT-TTF]·Ag·$(NO_3)_2$ based on the crystallographic analysis, and hence the BEDT-TTF unit should be present as a BEDT-TTF^{+}

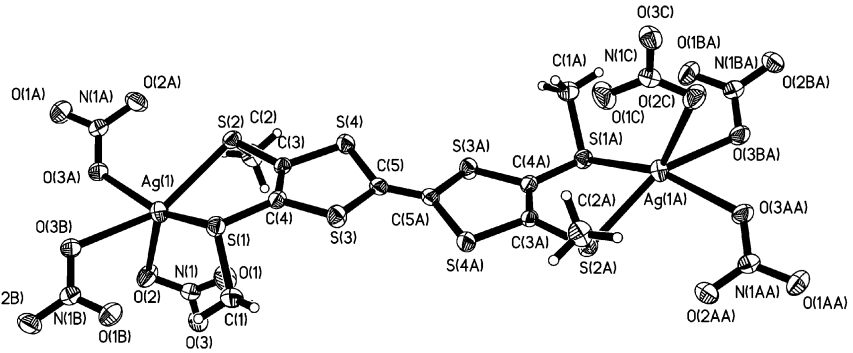


Fig. 1 TMTTF unit coordinated to two silver(I) ions in complex **1**.

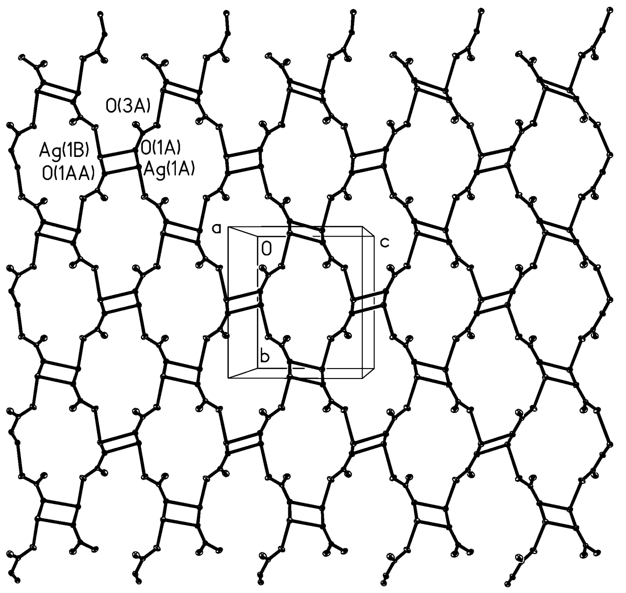


Fig. 2 Inorganic layer with a 4.16-net porous structure formed between silver(I) and nitrate ions in complex **1**.

cation, provided that the valences of the silver and nitrate ions in complex **2** are +1 and −1, respectively. Thus, the BEDT-TTF unit was oxidized[10] to generate the charge-transfer salt during the self-assembly process. In contrast, as stated above the TMTTF unit in complex **1** was not transformed into the corresponding charge-transfer salt, which may be due to the higher oxidation potential of TMTTF as compared to BEDT-TTF.[11] These results are indeed consistent with the fact that complex **2** is black while complex **1** is red in color. Moreover, the IR spectral data of complex **2** provide further evidence for the oxidation of BEDT-TTF units: as compared to the neutral BEDT-TTF (1408.9, 1283.9, 1260.4, 1173.4 cm^{-1}), the corresponding absorption bands in the range of 1500–1100 cm^{-1} are red-shifted for complex **2** (see Experimental). The crystal structure data (below) confirm the presence of BEDT-TTF$^+$ in complex **2**. Therefore, complex **2** is another new example of a complex of BEDT-TTF$^+$ cation with a metallic ion.

Fig. 4 shows the building unit of complex **2**. Selected bond lengths and angles are listed in Table 2. The silver(I) ion is coordinated by atoms S(7), O(11), O(21), and S(1^{iv}) (symmetrical operation: ^{iv} $-0.5+x$, $0.5-y$, $-0.5+z$, not shown in Fig. 4). The two outer $-CH_2-CH_2-$ units in the BEDT-TTF unit are in a chair (*trans*) conformation. The central TTF core of the BEDT-TTF unit in complex **2** forms dihedral angles of 12.4° and 10.4° with the planes of C(1), C(2), S(1), S(2) and S(7), S(8), C(9), C(10), respectively. The interatomic distance between the central carbon atoms of the BEDT-TTF unit can be used as a diagnostic test for the determination of the charge state of the donor: 1.32 Å in neutral BEDT-TTF and 1.38 Å in the BEDT-TTF$^+$ cation.[5] The present central double bond [C(5)–C(6)] distance is 1.38 Å, which indicates the presence of BEDT-TTF$^+$, in accordance with the formula of complex **2**. The bond lengths of Ag(1)–S(1^{iv}) and Ag(1)–S(7) are 2.6917(10) and 2.7295(10) Å, respectively, which are comparable to those of silver(I) and sulfur bonds in complex **1** and other silver(I) complexes. These bond lengths suggest the formation of Ag–S coordination bonds in complex **2**, despite the positive charge on the BEDT-TTF molecules, which would lead to an electrostatic repulsion between the metal and the ligand ions.

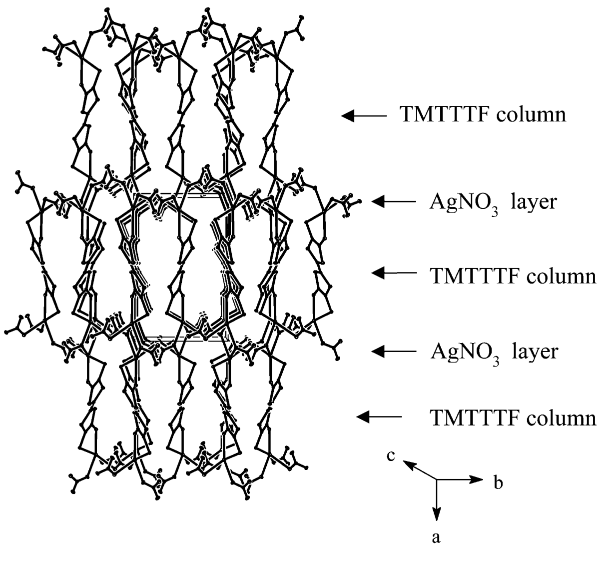


Fig. 3 3D framework of complex **1**; methyl groups are omitted for clarity.

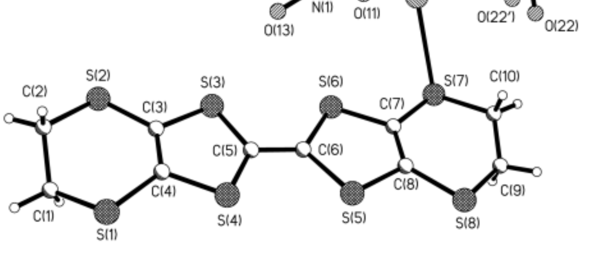


Fig. 4 Asymmetric unit of complex **2**.

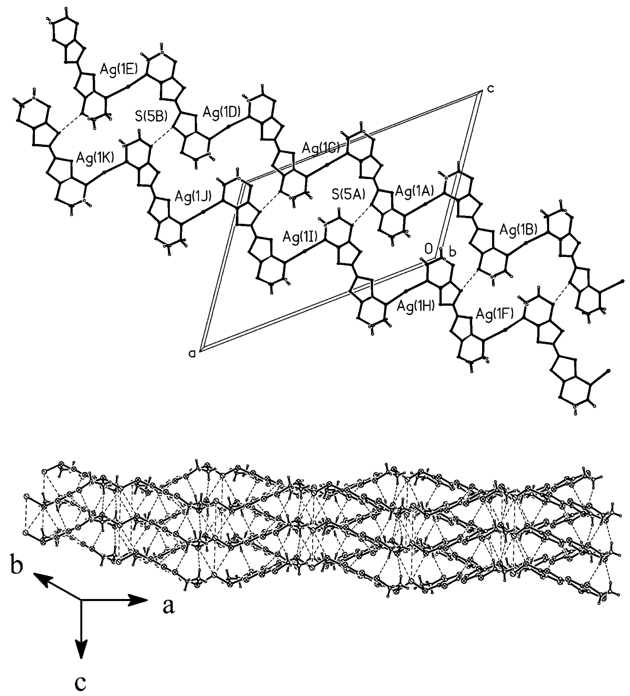


Fig. 5 1D "Zig-zag" chain structure and inter-chain arrangements in complex **2**.

The atoms Ag(1) and S(1) shown in Fig. 4 are further connected with another sulfur atom of a neighboring BEDT-TTF unit and another silver(I) ion, respectively, to form an extended one dimensional "zig-zag" chain as manifested in Fig. 5. The inter-chain arrangement in the crystal lattice is also displayed in Fig. 5. Obviously, columns consisting of BEDT-TTF units from neighboring chains are formed along the *c* axis. Short S–S contacts in the columns are found: S(5)–S(2)^{v}, 3.497 Å (symmetry operation: ^{v} $x, 1-y, -0.5+z$); S(8)–S(3)^{vi}, 3.465 Å (symmetry operations: ^{vi} $x, -y, -0.5+z$). Besides, there are also short interatomic distances between sulfur atoms and silver(I) ions (4.023 Å) and between silver(I) ions (4.273 Å) of adjacent chains.

Electrical conductivity

Complex 1. As anticipated, complex **1** is an insulator. After treatment by iodine vapor for 4 days, red crystals of **1** turned black with the loss of surface gloss. The resulting black complex was characterized by X-ray photoelectron spectroscopy (XPS). Three different binding energies of for S(2P$_{3/2}$) (163.49, 164.89 and 168.41 eV) with an approximate ratio of 61 : 20 : 19 were observed for this black complex, indicating the presence of three types of sulfur atoms. But, only one binding energy of S(2P$_{3/2}$) (163.38 eV) was detected in complex **1**. As compared to complex **1**, the doped complex shows one S(2P$_{3/2}$) binding energy (163.49 eV) that varies little, while the other two are shifted to higher energy. This result suggests the formation of a charge-transfer salt after the oxidation of complex **1** with iodine. In the IR spectrum of this black complex, two bands positioned at 1399 and 1335 cm^{-1} were observed. By comparison with the central C=C stretching frequency of the TMTTTF unit in complex **1** (1413 cm^{-1}), these two bands may arise from the neutral TMTTTF units and TMTTF$^{\bullet+}$ radical cations, respectively. Thus, only some of the TMTTTF electron donor molecules were oxidized after the treatment with iodine, which may be caused by a slow reaction rate, owing to gas–solid reaction characteristics. The composition of this charge-transfer salt was determined to be $[C_{10}H_{12}Ag_2N_2O_6S_8]\cdot I_{1.1}$ based on the result of elemental analysis.

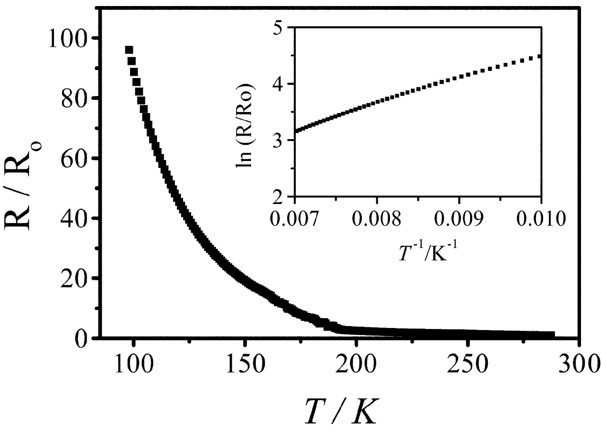


Fig. 6 Temperature dependence of the resistance of complex **1** after treatment with iodine; the inset shows the corresponding plot of ln(R/R_o) *versus* the inverse of temperature.

The conductivity of this charge-transfer salt was measured with the four-probe method, and the temperature dependence of the resistance is given in Fig. 6. Its room temperature conductivity was determined to be 4.5×10^{-3} S cm^{-1}. From room temperature to about 200 K, its electrical resistance varies very little. But, when the temperature is lowered further, the electrical resistance increases strongly, showing semiconducting behavior with the activation energy being about 0.08 eV. The conductivity of complex **1** after doping by iodine may be due to the TMTTTF$^{\bullet+}$/TMTTTF$^{\bullet+}$ and/or TMTTTF$^{\bullet+}$/TMTTTF interactions in the crystal lattice.

Complex 2. The room temperature conductivity of the crystals of complex **2** was measured to be 2.1×10^{-3} S cm^{-1}, and the temperature dependence of the resistance is shown in Fig. 7. From 300–150 K the resistance varies very little with temperature. But, below 150 K, it increases upon lowering the temperature further, typical of semiconducting behavior. The inset of Fig. 7 displays the corresponding plot of ln(R/R_o) *versus* the inverse of temperature, from which the activation energy was estimated to be 0.03 eV for the crystals of complex **2**.

It is well established that most organic conductors are based on charge-transfer salts or radical cation salts with a partial degree of charge transfer in particular for those derived from TTF derivatives. Thus, the low conductivity of complex **2** is mainly due to the fact that all BEDT-TTF units exist as BEDT-TTF^{+} cations in complex **2**.

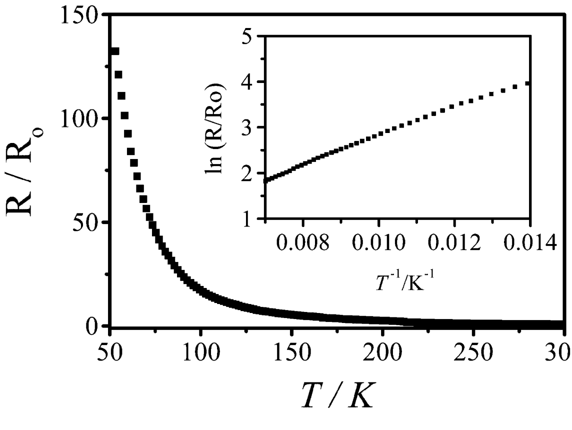


Fig. 7 Temperature dependence of the resistance of complex **2**; the inset shows the corresponding plot of ln(R/R_o) *versus* the inverse of temperature.

Summary

Two new silver(I) complexes of TTF derivatives are presented, one with TMTTTF showing an infinite 3D framework with an unprecedented 4.16 porous layer of silver(I) nitrate, and the other with BEDT-TTF forming a 1D extended "zig-zag" chain, in which silver(I) is coordinated to BEDT-TTF$^+$ cations. Further investigations include the preparation of TTF derivatives featuring other ligands such as pyridine and employment of paramagnetic ions in the self-assembly processes with the hope to generate new complexes, which not only will show novel structural characteristics, but also display interesting electrical and magnetic properties.

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8 Because of these disordered atoms, the nitrogen and oxygen atoms of the nitrate ions are treated isotropically for the structural refinement, and thermal parameters of atoms N(2) and O(13′) are relatively large.

9 C. Katayama, M. Honda, H. Kumagai, J. Tanaka, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2272.

10 The oxidizing reagent for BEDT-TTF in the synthesis of complex **2** should be $AgNO_3$.

11 The first oxidation potentials of BEDT-TTF and TMTTTF were determined to be 0.47 V (*vs.* SCE) and 0.64 V (*vs.* SCE), respectively, in 1,2-dichloroethane.