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Crystal Structure and Physical Properties of a Metallic Charge-Transfer Salt: $(BEDT\text{-}TTF)_2Ag(CN)_2.H_2O$

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Abstract

A new organic salt, bis[3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium] dicyanoargentate(I) monohydrate $[(BEDT\text{-}TTF)_2Ag(CN)_2.H_2O]$ (I), has been synthesized and its crystal structure and physical properties determined. The structure of (I) is different from those of the superconducting (β), metallic (β'') and insulating (β' and α') phases of anhydrous $(BEDT\text{-}TTF)_2X$, where X is a triatomic monoanion, but is similar to the newly found superconducting salts κ-$(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$. Crystal data for (I): $[C_{10}H_8S_8]_2[Ag(CN)_2].H_2O$, $M_r = 947{\cdot}2$, monoclinic, $P2_1$, $a = 12{\cdot}593\,(3)$, $b = 8{\cdot}642\,(1)$, $c = 16{\cdot}080\,(3)$ Å, $\beta = 109{\cdot}33\,(2)°$, $U = 1651{\cdot}2\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}905$ g cm^{-3}, Mo $K\alpha$ X-radiation (graphite monochromator), $\lambda = 0{\cdot}71069$ Å, $\mu = 16{\cdot}03$ cm^{-1}, $F(000) = 950$, $T = 298$ K, $R\,(wR) = 0{\cdot}033\,(0{\cdot}034)$ for 3884 unique observed $[F > 2\sigma(F)]$ data. The anion array consists of linear chains of three-coordinate Ag atoms linked by H_2O to form layers parallel to the BEDT-TTF layers, with which they form alternating stacks parallel to **c**. (I) is metallic over the temperature range 150–300 K. The EPR spectrum at 295 K consists of a single line at $g = 2{\cdot}007\,(3)$, with a peak-to-peak width H_{pp} of 70 G (0·007 T). Between 50 and 300 K an activated spin susceptibility with $E_a = 0{\cdot}01$ eV is observed.

Introduction

The discovery of superconductivity ($T_c = 1{\cdot}4$ K at ambient pressure) in β-$(BEDT\text{-}TTF)_2I_3$, a salt of the donor radical cation BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene (Yagubskii, Shchegolev, Lauklin, Konovich, Karatsovnik, Zvarykina & Buranov, 1984) triggered intense activity in the search for higher-temperature organic superconductors. A clear strategy for the design of new materials of this type is to synthesize compounds having the same basic structure and stoichiometry but with different lattice parameters. Such an approach is especially suitable for making correlations between structure and properties. From a chemical point of view, this aim can be achieved in several ways: (*a*) by replacing the S atoms in BEDT-TTF by Se, thus allowing larger p_π–p_π overlap, (*b*) by introducing a vinylene group instead of the ethylene group in the BEDT-TTF molecule, thus increasing the planarity of the donor which may result in closer S—S contacts, and (*c*) by changing the anions. The first two possibilities have been attempted by several groups but without much enhancement in T_c [see, for example, *Proceedings of the International Conference on Synthetic Metals* (1987, 1988)]. The third possibility has been successful in producing another three phases with higher T_c than 1·4 K, namely: β-$(BEDT\text{-}TTF)_2IBr_2$ 2·8 K (Williams, Wang, Beno, Emge, Sowa, Copps, Behroozi, Hall, Carlson & Crabtree, 1984); β-$(BEDT\text{-}TTF)_2AuI_2$ 5·0 K (Talham, Kurmoo, Day, Obertelli, Parker & Friend, 1986; Carlson, Crabtree, Nunez, Wang, Beno, Geiser, Firestone, Webb & Williams, 1986); and $(BEDT\text{-}TTF)_2Cu(SCN)_2$ 10·4 K (Urayama, Yamochi, Saito, Nozawa, Sugano, Kinoshita, Sato, Oshima, Kowamoto & Tanaka, 1988). Numerous linear anions have been tested for this purpose, covering a range of lengths from 7·8 to 10·1 Å, including anions with different atomic polarizabilities.† This substantial effort has produced a whole gamut of salts comprising several stoichiometries, structures, and hence physical properties.

In the present paper, we report the synthesis, crystal structure and physical properties of a new salt, $(BEDT\text{-}TTF)_2Ag(CN)_2.H_2O$ (I). (I) is among no less than five different products obtained during the electrocrystallization of BEDT-TTF with [*n*-

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† $CuCl_2$, 7·8; AuI_2, 8·1; $CuBr_2$, 8·4; ICl_2, 8·7; ClIBr, 9·0; $Ag(CN)_2$, 9·2; $Au(CN)_2$, 9·2; $AuBr_2$, 9·3; IBr_2, 9·3; AuI_2, 9·4; I_2Br, 9·7; and I_3, 10·1 Å.

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Table 1. *Summary of data for BEDT-TTF (ET) salts of silver cyanide*

	$(ET)_2Ag(CN)_2.H_2O$[a]	α'-$(ET)_2Ag(CN)_2$[b]	$(ET)_2Ag(CN)_2$[c]	$(ET)_2Ag(CN)_2$[c]	$(ET)Ag_4(CN)_5$[d]	$(ET)_2Cu(NCS)_2$[e]
Space group	$P2_1$	$P2/n$	$P2_12_12$	$P2_1/n$	$Fddd$	$P2_1$
a (Å)	12·595 (3)	7·956 (2)	9·519 (2)	10·996 (1)	13·24 (1)	16·248 (5)
b (Å)	8·642 (1)	6·732 (3)	4·952 (1)	4·281 (1)	19·48 (2)	8·440 (2)
c (Å)	16·080 (3)	30·738 (8)	33·927 (7)	34·093 (5)	19·62 (2)	13·124 (5)
β (°)	109·33 (2)	90·05 (1)		93·13 (2)		110·30 (3)
Z	2	2	2	2	8	2
V (Å^3)	1651·2 (5)	1646·3 (6)	1599·3 (6)	1602·4 (5)	5060 (8)	1688·0 (9)
Conductivity	Metal	Semiconductor	Metal	Metal–insulator	Semimetal	Superconductor

References: (*a*) this work, (*b*) Beno *et al.* (1986), (*c*) Stringer (1988), (*d*) Geiser *et al.* (1987), (*e*) Urayama, Yamochi, Saito, Nozawa *et al.* (1988).

$Bu_4N][Ag(CN)_2]$ in either dichloromethane or tetrahydrofuran (Table 1), and the second to be shown to have three-coordinate Ag atoms and a polymeric two-dimensional anion sublattice. However, unlike α'-(BEDT-TTF)$_2$Ag(CN)$_2$ (Beno, Firestone, Leung, Sowa, Wang & Williams, 1986; Parker, Friend, Kurmoo & Day, 1989; Obertelli, Friend, Talham, Kurmoo & Day, 1989), which is a one-dimensional semiconductor, or (BEDT-TTF)Ag$_4$(CN)$_5$, deduced from EPR measurements to be a three-dimensional metal, (I) is a two-dimensional metal, almost isotropic in its spin susceptibility within the basal plane.

Experimental

Synthesis

BEDT-TTF was prepared by standard routes and recrystallized twice from chloroform. [n-Bu$_4$N]-[Ag(CN)$_2$] was prepared by metathesis of (n-Bu$_4$N)NO$_3$ and K[Ag(CN)$_2$] in H_2O and recrystallized twice from ethanol. All starting materials gave satisfactory chemical analyses. CH_2Cl_2 (h.p.l.c. grade, BDH) was distilled from CaH_2 and chromatographed through neutral alumina prior to use. Crystals were obtained by electrocrystallization (Pt electrodes, 3 μA, 295 K) of BEDT-TTF (10 mg) and [n-Bu$_4$N][Ag(CN)$_2$] (250 mg) in CH_2Cl_2 (30 ml) for 7–10 days. (I) was obtained as a minor product among other phases, five of which have now been identified and characterized (Kurmoo, Talham, Pritchard, Day, Stringer & Howard, 1988; Geiser, Wang, Williams, Venturini, Kwak & Whangbo, 1987; Stringer, 1988). The crystals of (I) were first identified by X-ray crystal structure analysis and later by their morphology as long, black four-sided needles.

X-ray diffraction

Lattice parameters were derived from the setting angles ($18{\cdot}6 < 2\theta < 30{\cdot}3°$) of 15 centred reflections. Diffraction intensities were recorded on a Nicolet $P3/m$ diffractometer from a crystal of size 0·33 × 0·95 × 0·15 mm, giving 4075 unique data for $\omega/2\theta$ scans in the range 3–55°. Minumum/maximum hkl recorded were $0\,\overline{11}\,\overline{20}/16\;0\;20$. Three standard reflection intensities were checked every 100 hkl data; variations of less than 3·8% were observed. Lorentz, polarization and absorption corrections were applied, the latter by numerical methods (*SHELXTL*; Sheldrick, 1981) given the zone faces ⟨100⟩⟨010⟩⟨001⟩ and minimum/maximum transmission factors of 0·56/0·83. Hydrogen atoms were included at calculated positions, except for those of the water molecule which were located and refined isotropically, giving H—O 0·87 (6) Å and H—O—H 104·0 (3)°. All scattering factors, with corrections for anomalous scattering, were taken from *International Tables for X-ray Crystallography* (1974). 3884 data with $F > 2\sigma(F)$ were used in final refinement by the block-cascade least-squares method (*SHELXTL*) to $R\,(wR) = 0{\cdot}033\ (0{\cdot}034)$ where $w^{-1} = [\sigma^2(F) + g|F^2|]$, $g = 0{\cdot}0008$; $S = 1{\cdot}11$. The final difference density calculation showed $\Delta\rho$ within $+0{\cdot}7$ and $-0{\cdot}5$ e Å^{-3}; the maximum Δ/σ was 0·03 in the last cycles. All computations were performed on a Data General S230 Eclipse computer.

Electron paramagnetic resonance

The electron paramagnetic resonance (EPR) of single crystals (0·5 × 0·3 × 0·2 mm) was measured on a Varian E-109 reflection spectrometer at 9·19 GHz with 100 KHz field modulation and a helium gas flow cryostat. Crystals were mounted on spectrosil rods using silicone grease. A home-built goniometer was used for rotation experiments.

Conductivity

Conductivity was measured by four-probe a.c. (110 Hz) or two-probe d.c. techniques. Contacts were made with silver paint along the long axis (**b**) of the crystal.

Results and discussion

Crystal and molecular structure

The derived positional and equivalent thermal parameters of all non-hydrogen atoms in (I) are given in Table 2* and the numbering scheme is shown in Fig. 1. The bond distances and angles are listed in Table 3. The structure of (I) consists of dimers of two crystallographically independent BEDT-TTF molecules. Within a dimer, the BEDT-TTF molecules are arranged face-to-face but slipped with respect to one another (Fig. 3). Intermolecular S—S distances within the dimer lie in the range 3·7–3·8 Å (Fig. 2). The dihedral (twist) angle, between any two halves of the BEDT molecules, is very small ($< 0·5°$). Neighbouring dimers are not stacked in the usual fashion common to the α- and β-phase salts. In the latter, the planes of the BEDT-TTF molecules are parallel to one another within each stack. In contrast in (I), the planes of neighbouring dimers are almost perpendicular to each other. This represents a significant difference from the superconducting β phases (Williams *et al.*, 1984), the metallic β'' phase (Kurmoo, Talham, Day, Parker, Friend, Stringer & Howard, 1987), or the semiconducting α' phases of (BEDT-TTF)$_2X$ (Beno *et al.*, 1986; Parker *et al.*, 1989) for a wide range of linear triatomic anions (X). However, it is closely similar to both newly discovered κ-(BEDT-TTF)$_2$I$_3$ (Kobayashi, Kato, Kobayashi, Moriyama, Nishio, Kajita & Sasaki, 1987; Kato, Kobayashi, Kobayashi, Moriyama, Nishio, Kajita & Sasaki, 1987; Kajita, Nishio, Moriyama, Sasaki, Kato, Kobayashi & Kobayashi, 1987) and to (BEDT-TTF)Cu(NCS)$_2$ (Urayama, Yamochi, Saito, Nozawa *et al.*, 1988) which become superconducting at 3·6 and 10·4 K, respectively. There are several other examples of BEDT-TTF salts where face-to-face stacking is not observed, most of which are semiconducting, *viz* ε-(BEDT-TTF)$_2$I$_3$(I$_8$)$_{0·5}$ (semiconducting) (Shibaeva, Lobkovskaya, Yagubskii & Kostyuchenko, 1986); (BEDT-TTF)I$_3$(TCE)$_{0·33}$ (TCE = 1,1,2-trichloroethane; metal–insulator transition at ~160 K, $\sigma_{\rm RT}$ = 10–20 S cm^{-1}, E_a = 0·13 V) (Shibaeva, Lobkovskaya, Kaminskii, Lindemann & Yagubskii, 1986); (BMDT-TTF)$_2$Au(CN)$_2$ [BMDT-TTF = bis(methylenedithio)tetrathiafulvalene; metal–insulator transition at 76 K, $\sigma_{\rm RT}$ = 300 S cm^{-1}] (Nigrey, Morosin, Kwak, Venturini & Baughman, 1986); (BMDT-TTF)$_3$(PF$_6$)DCE [DCE = 1,2-dichloroethane; semiconducting, E_a = 0·11 eV (115–205 K), 0·20 eV (205–300 K), $\sigma_{\rm RT}$ = 10 S cm^{-1}] (Kato, Kobayashi, Sasaki & Kobayashi, 1984); and (BEDSe-TSeF)-(AuBr$_2$) [BEDSe-TSeF = bis(methylenediseleno)-tetraselenafulvalene; semiconducting, $\sigma_{\rm RT}$ = 0·14 S cm^{-1}, E_a = 0·13 eV] (Kato, Kobayashi, Kobayashi, Mori & Inokuchi, 1987). There are several short S—S distances in the range 3·5–3·8 Å between the dimers in (I) (Fig. 3), which are thereby formed into two-dimensional arrays, separated by layers of anions.

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
Ag	8517 (1)	10000	10055 (1)	51 (1)
C(1*b*)	7112 (4)	8757 (6)	10086 (3)	45 (2)
N(1*b*)	6292 (4)	8200 (8)	10101 (3)	68 (2)
C(2*b*)	9514 (4)	11944 (6)	10086 (3)	43 (1)
N(2*b*)	10093 (4)	12947 (6)	10105 (3)	56 (2)
O	4052 (5)	9690 (7)	10033 (4)	91 (3)
C(1)	8758 (3)	5177 (5)	4652 (2)	32 (1)
C(2)	8480 (3)	5162 (5)	5408 (2)	31 (1)
S(3)	8113 (1)	6482 (1)	3808 (1)	35 (1)
S(4)	7436 (1)	6374 (1)	5530 (1)	36 (1)
C(5)	8861 (3)	5878 (5)	3123 (2)	33 (1)
C(6)	7697 (3)	5916 (5)	6640 (2)	30 (1)
C(7)	9608 (3)	4728 (5)	3425 (2)	33 (1)
C(8)	8486 (3)	4833 (5)	6997 (2)	31 (1)
S(9)	9763 (1)	3989 (1)	4471 (1)	36 (1)
S(10)	9109 (1)	3952 (1)	6293 (1)	33 (1)
S(11)	8508 (1)	6867 (2)	2119 (1)	43 (1)
S(12)	6885 (1)	6975 (2)	7129 (1)	45 (1)
C(13)	9086 (4)	5572 (6)	1494 (3)	46 (2)
C(14)	7552 (5)	6504 (7)	8276 (3)	54 (2)
C(15)	10282 (4)	5093 (7)	1976 (3)	51 (2)
C(16)	7884 (4)	4838 (7)	8472 (3)	47 (2)
S(17)	10466 (1)	3844 (2)	2905 (1)	50 (1)
S(18)	8993 (1)	4202 (2)	8086 (1)	42 (1)
C(1*a*)	6488 (3)	2373 (5)	4697 (2)	30 (1)
C(2*a*)	6201 (3)	2373 (5)	5448 (2)	29 (1)
S(3*a*)	5876 (1)	3571 (1)	3794 (1)	33 (1)
S(4*a*)	5227 (1)	3631 (1)	5638 (1)	33 (1)
C(5*a*)	6566 (4)	2703 (5)	3129 (3)	34 (1)
C(6*a*)	5415 (3)	2939 (5)	6703 (3)	34 (1)
C(7*a*)	7325 (3)	1589 (5)	3502 (3)	32 (1)
C(8*a*)	6120 (3)	1736 (5)	6997 (2)	32 (1)
S(9*a*)	7504 (1)	1101 (2)	4592 (1)	39 (1)
S(10*a*)	6792 (1)	1032 (1)	6276 (1)	37 (1)
S(11*a*)	6159 (2)	3361 (2)	2048 (1)	76 (1)
S(12*a*)	4651 (1)	3902 (2)	7270 (1)	51 (1)
C(13*a*)	6691 (5)	1856 (8)	1530 (3)	64 (2)
C(14*a*)	4562 (4)	2377 (6)	8005 (3)	42 (2)
C(15*a*)	7871 (5)	1409 (8)	1997 (3)	63 (2)
C(16*a*)	5701 (4)	1774 (6)	8583 (3)	40 (1)
S(17*a*)	8151 (1)	514 (2)	3044 (1)	50 (1)
S(18*a*)	6472 (1)	740 (2)	7990 (1)	44 (1)

The anion layers in (I) are made up of Ag(CN)$_2$ and water molecules (Fig. 4). The Ag atoms are coordinated by two C atoms and one N atom instead of the linear geometry expected for a closed-shell [Ag(CN)$_2$]$^-$ unit and observed in α'-(BEDT-

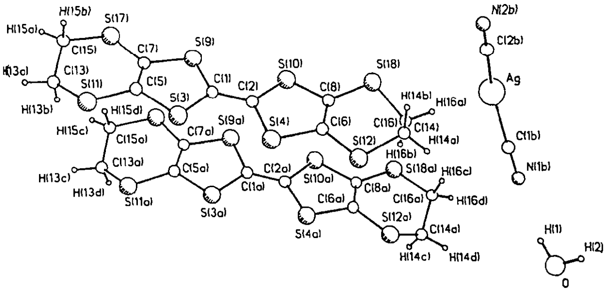

Fig. 1. Numbering scheme of atoms.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52501 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and bond angles* (°)

$Ag(CN)_2$							
Ag—C(1*b*)	2·084 (5)	Ag—C(2*b*)	2·088 (5)	C(2*b*)—N(2*b*)	1·127 (7)	Ag—N(2*b*)	2·564 (6)
		C(1*b*)—N(1*b*)	1·147 (8)				
BEDT-TTF		BEDT-TTF(*a*)		BEDT-TTF		BEDT-TTF(*a*)	
C(1)—C(2)	1·372 (6)	C(1*a*)—C(2*a*)	1·370 (6)	C(1)—S(3)	1·744 (4)	C(1*a*)—S(3*a*)	1·742 (4)
C(1)—S(9)	1·727 (4)	C(1*a*)—S(9*a*)	1·737 (4)	C(2)—S(4)	1·742 (4)	C(2*a*)—S(4*a*)	1·741 (4)
C(2)—S(10)	1·732 (4)	C(2*a*)—S(10*a*)	1·736 (4)	S(3)—C(5)	1·748 (5)	S(3*a*)—C(5*a*)	1·755 (5)
S(4)—C(6)	1·750 (4)	S(4*a*)—C(6*a*)	1·754 (4)	C(5)—C(7)	1·343 (6)	C(5*a*)—C(7*a*)	1·349 (6)
S(5)—S(11)	1·750 (4)	C(5*a*)—S(11*a*)	1·737 (4)	C(6)—C(8)	1·347 (5)	C(6*a*)—C(8*a*)	1·348 (6)
C(6)—S(12)	1·741 (5)	C(6*a*)—S(12*a*)	1·740 (5)	C(7)—S(9)	1·749 (4)	C(7*a*)—S(9*a*)	1·743 (4)
C(7)—S(17)	1·747 (5)	C(7*a*)—S(17*a*)	1·730 (5)	C(8)—S(10)	1·751 (4)	C(8*a*)—S(10*a*)	1·754 (5)
C(8)—S(18)	1·741 (4)	C(8*a*)—S(18*a*)	1·737 (4)	S(11)—C(13)	1·809 (6)	S(11*a*)—C(13*a*)	1·790 (7)
S(12)—C(14)	1·802 (5)	S(12*a*)—C(14*a*)	1·799 (5)	C(13)—C(15)	1·507 (7)	C(13*a*)—C(15*a*)	1·477 (8)
C(14)—C(16)	1·503 (8)	C(14*a*)—C(16*a*)	1·520 (6)	C(15)—S(17)	1·795 (6)	C(15*a*)—S(17*a*)	1·780 (6)
C(16)—S(18)	1·791 (6)	C(16*a*)—S(18*a*)	1·807 (5)				
$Ag(CN)_2$							
C(1*b*)—Ag—C(2*b*)	157·3 (2)	C(1*b*)—Ag—N(2*b*′)	105·0 (2)	Ag—C(2*b*)—N(2*b*)	176·7 (5)	Ag—N(2*b*′)—C(2*b*′)*	170·7 (5)
C(2*b*)—Ag—N(2*b*′)	97·7 (2)	Ag—C(1*b*)—N(1*b*)	173·7 (5)				
BEDT-TTF		BEDT-TTF(*a*)		BEDT-TTF		BEDT-TTF(*a*)	
C(2)—C(1)—S(9)	124·0 (3)	C(2*a*)—C(1*a*)—S(9*a*)	120·2 (3)	C(2)—C(1)—S(3)	120·4 (3)	C(2*a*)—C(1*a*)—S(3*a*)	124·2 (3)
C(1)—C(2)—S(4)	121·2 (3)	C(1*a*)—C(2*a*)—S(4*a*)	124·2 (3)	S(3)—C(1)—S(9)	115·6 (2)	S(3*a*)—C(1*a*)—S(9*a*)	115·6 (2)
S(4)—C(2)—S(10)	115·3 (2)	S(4*a*)—C(2*a*)—S(10*a*)	115·5 (2)	C(1)—C(2)—S(10)	123·5 (3)	C(1*a*)—C(2*a*)—S(10*a*)	120·4 (3)
C(2)—S(4)—C(6)	94·9 (2)	C(2*a*)—S(4*a*)—C(6*a*)	94·8 (2)	C(1)—S(3)—C(5)	95·1 (2)	C(1*a*)—S(3*a*)—C(5*a*)	94·7 (2)
S(3)—C(5)—S(11)	114·2 (2)	S(3*a*)—C(5*a*)—S(11*a*)	115·3 (2)	S(3)—C(5)—C(7)	116·8 (3)	S(3*a*)—C(5*a*)—C(7*a*)	117·0 (3)
S(4)—C(6)—C(8)	117·0 (3)	S(4*a*)—C(6*a*)—C(8*a*)	117·7 (3)	C(7)—C(5)—S(11)	129·0 (4)	C(7*a*)—C(5*a*)—S(11*a*)	127·6 (4)
C(8)—C(6)—S(12)	129·3 (3)	C(8*a*)—C(6*a*)—S(12*a*)	126·9 (3)	S(4)—C(6)—S(12)	113·7 (2)	S(4*a*)—C(6*a*)—S(12*a*)	115·4 (2)
C(5)—C(7)—S(17)	128·3 (3)	C(5*a*)—C(7*a*)—S(17*a*)	129·1 (3)	C(5)—C(7)—S(9)	117·4 (3)	C(5*a*)—C(7*a*)—S(9*a*)	117·2 (4)
C(6)—C(8)—S(10)	116·9 (3)	C(6*a*)—C(8*a*)—S(10*a*)	116·2 (3)	S(9)—C(7)—S(17)	114·3 (2)	S(9*a*)—C(7*a*)—S(17*a*)	113·7 (2)
S(10)—C(8)—S(18)	114·9 (2)	S(10*a*)—C(8*a*)—S(18*a*)	113·8 (2)	C(6)—C(8)—S(18)	128·2 (3)	C(6*a*)—C(8*a*)—S(18*a*)	130·0 (4)
C(2)—S(10)—C(8)	95·0 (2)	C(2*a*)—S(10*a*)—C(8*a*)	95·6 (2)	C(1)—S(9)—C(7)	95·1 (2)	C(1*a*)—S(9*a*)—C(7*a*)	95·2 (2)
C(6)—S(12)—C(14)	101·5 (2)	C(6*a*)—S(12*a*)—C(14*a*)	99·2 (2)	C(5)—S(11)—C(13)	100·6 (2)	C(5*a*)—S(11*a*)—C(13*a*)	101·3 (2)
S(12)—C(14)—C(16)	115·7 (4)	S(12*a*)—C(14*a*)—C(16*a*)	113·7 (3)	S(11)—C(13)—C(15)	113·7 (3)	S(11*a*)—C(13*a*)—C(15*a*)	115·0 (4)
C(14)—C(16)—S(18)	114·6 (4)	C(14*a*)—C(16*a*)—S(18*a*)	114·2 (3)	C(13)—C(15)—S(17)	115·1 (4)	C(13*a*)—C(15*a*)—S(17*a*)	116·4 (5)
C(8)—S(18)—C(16)	100·6 (2)	C(8*a*)—S(18*a*)—C(16*a*)	102·8 (2)	C(7)—S(17)—C(15)	101·9 (2)	C(7*a*)—S(17*a*)—C(15*a*)	102·2 (3)

*Atom *X*(*nb*′) refers to that atom generated by the symmetry operator (−*x*, 0·5 + *y*, − *z*) producing adjacent molecules (1 + *y*) in the packing arrangement shown in Fig. 5(*a*).

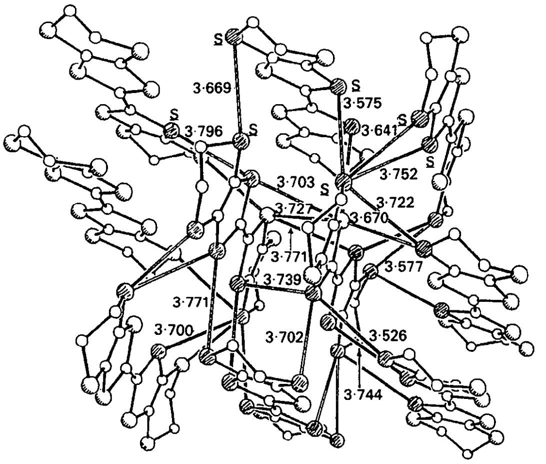


Fig. 2. Short S—S contacts (Å) in BEDT-TTF layers. Sulfur atoms involved in close contacts are shaded for emphasis.

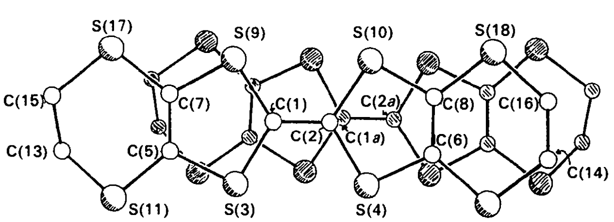


Fig. 3. Overlap of BEDT-TTF molecules within a dimer. Atoms of lower molecule (*a*) are shaded for clarity.

TTF$)_2$Ag(CN$)_2$ (Beno *et al.*, 1986). The Ag, C and N atoms form chains parallel to the *a* axis, which are, in turn, cross-linked by water molecules through hydrogen bonds to the terminal N atoms of the cyanide groups, thus building up an almost planar

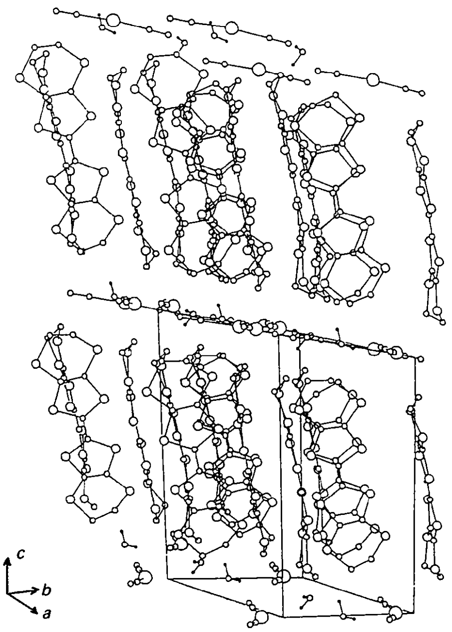


Fig. 4. Unit-cell contents of $(BEDT\text{-}TTF)_2Ag(CN)_2.H_2O$.

sheet of anions. A similar and unusual trigonally coordinated Cu atom has been observed recently in (BEDT-TTF)$_2$Cu(NCS)$_2$ (Urayama, Yamochi, Saito, Sato, Kowamoto, Tanaka, Mori, Maruyama & Inokuchi, 1988) wherein the Cu atom is linked to two NCS ligands through N and to the third through the S atom.

The approach of the N to the Ag results in a reduction of the normally linear C—Ag—C angle of Ag(CN)$_2$ to 157·3 (2)°. The sum of the three angles about Ag is exactly 360·0° indicating precise planarity of the C$_2$—Ag···N unit. The Ag—C bond lengths are equal within error [2·084 (5) and 2·088 (5) Å] {*cf.* 2·07 (2) Å for *M*[Ag(CN)$_2$].2H$_2$O, *M* = Ca or Sr (Rauge, Zabel, Meyer & Fischer, 1985)}. The Ag—N distance is 2·564 (6) Å. There are two distinguishable N atoms, one in van der Waals contact with the Ag atom and the other with the H atom of the water molecule. This results in two C—N bond lengths, 1·147 (8) and 1·127 (7) Å, respectively.

To our knowledge, such a polymeric form of silver cyanide has not been observed before. For example it is distinctly different from that found in (BEDT-TTF)Ag$_4$(CN)$_5$ (Geiser *et al.*, 1987). In the latter, the anion units can be considered as a 'necklace' of ten Ag and ten CN with two distinct Ag atoms, while the anionic unit in (I) is a small ring of three Ag atoms, four CN and two H$_2$O ligands, together with one N atom from a neighbouring chain and only one distinct Ag atom. The other main difference between (I) and (BEDT-TTF)Ag$_4$(CN)$_5$ is that, in the latter, the BEDT-TTF molecules are located within the anion 'necklaces', so that no stacking is observed but instead weak S···S interactions are present in a three-dimensional arrangement. In contrast, the layer structure is well defined in (I) with quite strong intralayer interactions. We believe this new structure represents the first truly two-dimensional isotropic system in the whole family of BEDT-TTF charge-transfer salts.

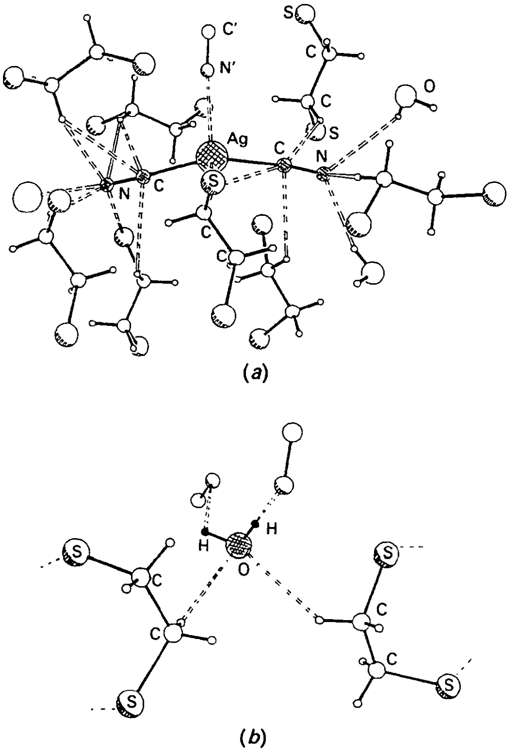
The conformation of the terminal $>$CH$_2$ groups in the BEDT-TTF molecules has been found to be responsible for the existence of two different phases of β-(BEDT-TTF)$_2$I$_3$ (Whangbo, Williams, Schultz, Emge & Beno, 1987). The phase in which the $>$CH$_2$ groups are disordered is a superconductor with T_c = 1·4 K, while the one in which they are ordered, obtained by application of 1·5 kbar (0·15 GPa) pressure, has T_c = 8·1 K (Creuzet, Creuzet, Jerome, Schweitzer & Keller, 1986). In the present case, the $>$CH$_2$ are ordered in both of the crystallographically independent molecules; in one they are in a *cis* conformation and in the other they adopt a *trans* conformation. Several specific anion–cation interactions are also observed. For example there are S···N contacts which are 0·09 Å less than the sum of van der Waals radii (Fig. 5*a*). There is also an indication of weak hydrogen bonding the O atom of the water molecules and the H atoms of the $>$CH$_2$ groups (Fig. 5*b*). The shortest C—H···O distance observed is 2·65 Å and the corresponding C—H···O angle is 138°. The closest N···H is 2·76 Å.

Conductivity

Some difficulties were encountered in measuring the electrical conductivity of (I). The contact resistances range from 50 Ω on some crystals to kΩ on others. The temperature dependence of the conductivity was metallic in the best crystals, while for others semiconducting behaviour was observed, with activation energy of about 0·01 eV. The crystals are very brittle, especially at low temperature, so that conductivity could not be measured below 150 K. No improvement resulted from the use of Au paint or evaporated Au contacts in place of Ag paint.

Electron paramagnetic resonance

EPR measurements were performed as a function of crystal angle and temperature (5–300 K). At room temperature the EPR is characterized by a single symmetric peak at g = 2·007 (3) and a peak-to-peak



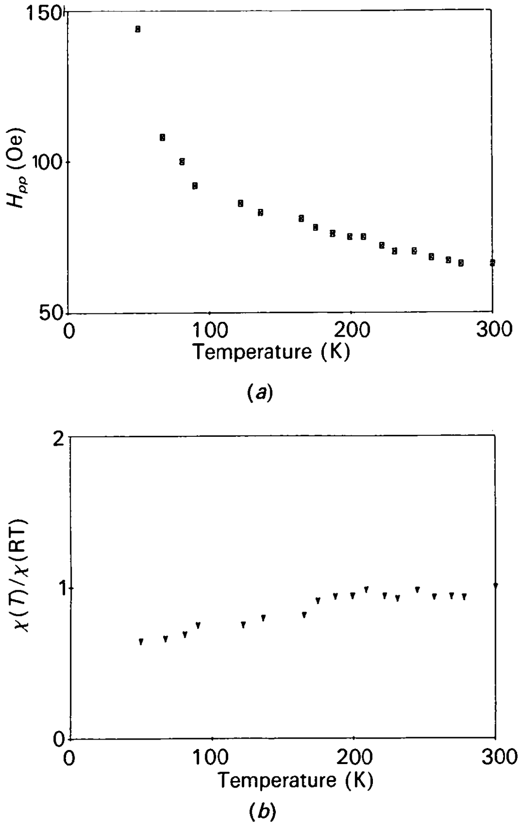
(*a*)

(*b*)

Fig. 5. Details of packing around (*a*) the [Ag(CN)$_2$] anion and (*b*) the H$_2$O molecule showing only part of proximal BEDT-TTF molecules. Central atoms in the coordination spheres are hatched.

width H_{pp} of about 70 G (0·007 T). Given that the anion is diamagnetic, the resonance originates from the conduction electrons. Also, its weakness indicates that the spins are not localized. Considering the thickness of the crystal used, the fact that the resonance is symmetrical and not Dysonian implies a room-temperature conductivity of less than 100 S cm^{-1}.

Rotation of the single crystal about its *b* axis reveals a 180° periodicity in the *g* value with $g_{\min}$ = 2·004 (1), $g_{\max}$ = 2·010 (1), $H_{pp,\min}$ = 63 G (0·0063 T), $H_{pp,\max}$ = 85 G (0·0084 T) and the ratio of the susceptibilities $\chi_{\text{spin,min}}/\chi_{\text{spin,max}}$ = 0·92. Relating these data to the crystallographic axes, we find that when H_0, the static field, is parallel to **b**, g = 2·004 (1), H_{pp} = 84 G (0·0084 T) and when it is perpendicular $g_{\min}$ = 2·004 (1), $g_{\max}$ = 2·011 (1), $H_{pp,\min}$ = 58 G (0·0058 T) and $H_{\text{pp,max}}$ = 74 G (0·0074 T). The ratio of the spin susceptibilities as the field is rotated about *b* does not exceed 1·3, *i.e.* the spin susceptibility is almost isotropic as the static field is rotated within the plane of the layers of orthogonal BEDT-TTF dimers.



(*a*)

(*b*)

Fig. 6. (*a*) Temperature dependence of the EPR linewidth (H_{pp}) for H_0 perpendicular (1Oe = 10^3 A m^{-1}). (*b*) Temperature dependence of the normalized spin susceptibility for H_0 perpendicular to **b**.

On cooling there is an increase in H_{pp} and a monotonic decrease in spin susceptibility (Fig. 6). The *g* values remain constant within experimental error. H_{pp} increases more steeply when the static field is parallel to the *b* axis. It is worth noting that H_{pp} is related to the electron relaxation time, which depends on the spin–lattice interaction. For a metal this parameter decreases with decreasing temperature since the mean free path of the carriers increases with decreasing lattice scattering. So, for the metallic BEDT-TTF salt, we anticipate a decrease in H_{pp} (Kurmoo, Talham & Day, 1989). In most metallic materials the temperature dependence of H_{pp} is related to that of the resistivity, but in the present case the reverse is observed. For a wide-band metal, the theoretical power law is T^2 at high temperature (300 K); in contrast, for (I) we find that H_{pp} is proportional of $T^{-0\cdot33\,(3)}$ from 100–300 K.

The spin susceptibility for H_0 parallel to the *b* axis is difficult to estimate because of the weak signal and large H_{pp}. With H_0 perpendicular to **b**, χ_{spin} decreases slowly with decreasing temperature (Fig. 6). Data were only available for the temperature range 50–300 K, owing to the weakness of the signal below 50 K and also the presence of paramagnetic impurity peaks. Analysis of the data between 50 and 300 K indicates an activated behaviour with an activation energy of 0·01 eV. This is analogous to the behaviour of $(\mathrm{BEDT\text{-}TTF})_3\mathrm{Cl}_2.2\mathrm{H}_2\mathrm{O}$ at ambient pressure. The latter is a metal from 300 to about 100 K, at which it undergoes a metal–insulator transition (Rosseinsky, Kurmoo, Talham, Day, Chasseau & Watkin, 1988). This transition is suppressed by a pressure of 15 kbar (1·5 GPa) to yield a superconducting state at *ca* 5 K (Kurmoo, Rosseinsky, Day, Auban, Kang, Jerome & Batail, 1988).

Concluding remarks

We have synthesized crystals of a new charge-transfer salt of BEDT-TTF, (I), which shows the same type of packing of BEDT-TTF molecules as in the newly discovered superconductors κ-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{I}_3$ (Kobayashi *et al.*, 1987) and $(\mathrm{BEDT\text{-}TTF})_2\mathrm{Cu(SCN)}_2$ (Urayama, Yamochi, Saito, Nozawa *et al.*, 1988). Unfortunately, the brittleness of the crystals has precluded a definitive determination of the electrical properties over a wide range of temperatures, but from 300 to 150 K the conductivity is metallic. In contrast, EPR data suggest low electrical conductivity and an activated spin susceptibility. The rotational variation of the EPR parameters, and their relation to the crystallographic axes indicate that within the plane of the BEDT-TTF layers the spin system is almost isotropic. The observation of water of crystallization in this phase and also in $(\mathrm{BEDT\text{-}TTF})_3\mathrm{Cl}_2.2\mathrm{H}_2\mathrm{O}$ (Rosseinsky *et al.*, 1988), proves that one can construct charge-transfer salts of BEDT-TTF with quite different donor packing motifs in the presence of water, especially if the anion is small and alone cannot stabilize salts of BEDT-TTF.

We thank the SERC for support.

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Studies in Werner Clathrates. 12.* Structures of Four Novel but Non-Clathrating Complexes

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Abstract

Compound (I), tetrakis(4-benzylpyridine)bis(isothiocyanato)nickel(II), $C_{50}H_{44}N_6NiS_2$, [Ni(NCS)$_2$(C$_{12}$H$_{11}$N)$_4$], $M_r = 851{\cdot}8$, monoclinic, Cc, $a = 9{\cdot}686\,(6)$, $b = 25{\cdot}015\,(10)$, $c = 17{\cdot}728\,(9)$ Å, $\beta = 90{\cdot}29\,(8)°$, $V = 4295{\cdot}2$ Å^3, $Z = 4$, $D_m = 1{\cdot}298$, $D_x = 1{\cdot}32$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 5{\cdot}47$ cm^{-1}, $F(000) = 2016$, $R = 0{\cdot}056$ for 2819 observed reflections. Compound (II), tetrakis(4-*tert*-butylpyridine)-

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* Part 11: Lavelle, Nassimbeni, Niven & Taylor (1989).

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