New packing type of the conducting layer in the structure of the organic semiconductor $(ET)_6[Pb_3Br_9PhClMe_2CO]$, the first ET-based lead-containing salt

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A new organic semiconductor, $(ET)_6[Pb_3Br_9PhClMe_2CO]$, which is the first radical cation salt based on bis(ethylenedithio)tetrathiafulvalene (ET) with a lead-containing anion, has been synthesized. The composition and crystal and molecular structure of this compound have been established by X-ray structural analysis. The crystal structure can be described as a layer structure. A new α''' type of packing of ET radical cations has been found in the conducting layer. The anionic layer consists of $[Pb_3Br_9^{3-}]_n$ polymeric anions and chlorobenzene and acetone solvate molecules bonded to polymeric anions through Br...H—C hydrogen bonds.

Key words: bis(ethylenedithio)tetrathiafulvalene (ET); lead halides; organic semiconductors, synthesis, crystal structure.

Radical cation salts of bis(ethylenedithio)tetrathiafulvalene (ET) with anions containing different metals[1] are characterized by a wide range of conducting properties including superconductivity.[2] In these compounds, ET can be not only a neutral molecule, a cation, or a radical cation, but a ligand as well.[3,4]

Once organic superconductors and organic metals based on ET salts with Hg-containing anions were obtained,[5—10] it was reasonable to attempt to synthesize ET salts with the elements closest to mercury in the periods and groups of the Periodic system. Previously,[11,12] we obtained ET salts with Cd-containing anions, $(ET)_4Cd_2I_6$ and $(ET)_2Cd_3I_6$, and studied their structures. The present work is devoted to study of the structure of an ET radical cation salt with a lead-containing anion, $(ET)_6[Pb_3Br_9PhClMe_2CO]$ (**1**). The composition, molecular formula, and crystal and molecular structure of **1** were established by X-ray structural analysis.

Experimental

Crystals of **1** were obtained on a Pt anode by electrochemical oxidation of a 10^{-3} *M* ET solution in a 8 : 5 chlorobenzene—acetone system for 10 days at room temperature using Bu_4NPbBr_3 and Bu_4NBr (10^{-1} and $0.8 \cdot 10^{-1}$ mol L^{-1}, respectively) as supporting electrolytes; $I = 0.5$ μA. The conductivity of **1**, $\sigma_{300} = 1\ \Omega^{-1}\ cm^{-1}$.

The crystallographic data are as follows: $(C_{10}H_8S_8)_6[Pb_3Br_9(C_6H_5Cl)(CH_3)_2CO]$, M = 3818.41, triclinic system, $a = 19.792(9)$ Å, $b = 17.517(9)$ Å, $c = 16.454(5)$ Å, $\alpha = 91.92(3)°$, $\beta = 79.49(3)°$, $\gamma = 97.40(4)°$, $V = 5561.9$ Å^3, the space group is $P\bar{1}$, $Z = 2$, $d_{calc} = 2.27$ g cm^{-3}, $F(000) = 2308$. The unit-cell parameters were refined by the least-squares method using reflection angles of 15 reflections automatically centered on a diffractometer. The compound crystallizes as black rhombus- or parallelogram-shaped plates. A 0.25×0.25×0.07-mm crystal was chosen for X-ray structural study.

Intensities of 13706 reflections, of which only 3225 reflections had $I > 2\sigma(I)$, were collected on an automated four-circle KM-4 diffractometer (Kuma diffraction, Poland) using $\omega/2\theta$ scanning technique and monochromated Mo-Kα radiation ($2\theta_{max} = 47.9°$). The structure was solved by the full-matrix least-squares method using the weighting scheme $w = 1/(\sigma^2(F) + 0.002566F^2)$ to $R = 0.054$ and $R_w = 0.055$. Hydrogen atoms were not located. Absorption by the crystal (μ(Mo-Kα) = 5.87 mm^{-1}) was calculated taking into account the habitus of the sample (in the framework of the SHELX-76 program[13]). Atomic coordinates and thermal parameters are given in Table 1. All calculations were performed on a PC AT-286 computer using the SHELX-76[13] and SHELX-86[14] program packages.

Results and Discussion

The crystal structure of **1** consists of layers (Fig. 1). The layers formed by ET radical cations alternate along the *a* axis of the crystal with layers formed by $[Pb_3Br_9]^{3-}$ anions and solvate molecules of chlorobenzene and acetone. Cationic and anionic layers are parallel to the *bc* plane. Interatomic distances and bond angles in the $[Pb_3Br_9 \cdot PhCl \cdot Me_2CO]^{3-}$ anion are given in Tables 2 and 3, respectively.

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Table 1. Coordinates for nonhydrogen atoms and equivalent isotropic temperature factors (B_{eq}) in the structure of $(ET)_6[Pb_3Br_9PhClMe_2CO]$

Atom	x	y	z	B_{eq}/Å^2
Pb(1)	0.5000	0.0000	0.5000	3.2
Pb(2)	0.5005(1)	0.1733(1)	0.6612(2)	3.5
Pb(3)	0.4870(1)	0.3450(1)	0.8244(1)	3.3
Pb(4)	0.5000	0.5000	1.0000	3.1
Br(1)	0.3895(3)	0.0518(3)	0.6300(3)	3.8
Br(2)	0.5888(3)	0.0372(4)	0.6326(4)	5.2
Br(3)	0.5442(3)	0.1736(3)	0.4715(4)	5.3
Br(4)	0.4528(3)	0.1688(3)	0.8489(4)	4.5
Br(5)	0.4071(3)	0.2958(3)	0.6825(3)	3.9
Br(6)	0.6070(3)	0.3098(3)	0.6986(3)	3.8
Br(7)	0.3728(3)	0.4114(3)	0.9526(3)	4.7
Br(8)	0.5651(3)	0.3544(3)	0.9622(4)	4.3
Br(9)	0.5420(3)	0.5152(3)	0.8112(4)	5.4
S(1)	0.2807(6)	0.0164(8)	0.0467(8)	3.7
S(2)	0.1273(5)	−0.0190(7)	0.0647(7)	2.9
S(3)	−0.0339(6)	−0.0771(8)	0.0774(7)	3.4
S(4)	−0.1750(6)	−0.1448(8)	0.0727(8)	3.7
S(5)	−0.2123(6)	−0.0647(8)	0.2728(7)	3.6
S(6)	−0.0624(6)	−0.0063(7)	0.2418(8)	3.6
S(7)	0.0989(7)	0.0574(8)	0.2260(8)	4.2
S(8)	0.2437(7)	0.1066(8)	0.2394(8)	3.7
S(9)	0.2308(6)	0.2756(8)	0.0615(7)	3.5
S(10)	0.0797(6)	0.2283(7)	0.0945(8)	3.3
S(11)	−0.0832(6)	0.1659(8)	0.1107(8)	3.5
S(12)	−0.2258(6)	0.1046(8)	0.1069(8)	3.7
S(13)	−0.2616(7)	0.2011(9)	0.2970(8)	4.2
S(14)	−0.1115(6)	0.2469(7)	0.2697(7)	2.5
S(15)	0.0544(6)	0.3088(7)	0.2527(7)	3.1
S(16)	0.2004(6)	0.3722(7)	0.2520(8)	3.5
S(17)	0.1612(7)	0.6145(8)	0.2426(8)	4.1
S(18)	0.0170(6)	0.5475(7)	0.2442(7)	3.4
S(19)	−0.1446(6)	0.4760(6)	0.2640(7)	2.5
S(20)	−0.2978(6)	0.4310(7)	0.2862(7)	3.5
S(21)	−0.2589(7)	0.3311(7)	0.1033(8)	4.1
S(22)	−0.1136(6)	0.3945(7)	0.1060(7)	3.4
S(23)	−0.0457(6)	0.4603(7)	0.0901(8)	3.4
S(24)	0.1961(6)	0.5078(7)	0.0592(8)	3.5
S(25)	0.2804(6)	0.8854(7)	0.2373(7)	3.1
S(26)	0.1339(6)	0.8355(7)	0.2301(8)	3.3
S(27)	−0.0289(6)	0.7710(7)	0.2441(7)	3.2
S(28)	−0.1733(6)	0.7033(7)	0.2817(7)	3.1
S(29)	−0.1398(6)	0.6195(7)	0.0884(8)	3.5
S(30)	0.0000(6)	0.6993(7)	0.0814(8)	3.5
S(31)	0.1606(6)	0.7660(7)	0.0651(7)	3.0
S(32)	0.3121(6)	0.8007(7)	0.0411(7)	3.2
S(33)	−0.1581(7)	0.0085(8)	0.5978(9)	4.2
S(34)	−0.0187(6)	0.0912(7)	0.5740(7)	2.7
S(35)	0.1392(6)	0.1639(7)	0.5615(7)	2.5
S(36)	0.2848(6)	0.1975(8)	0.5629(8)	4.0
S(37)	0.2959(6)	0.2622(8)	0.3611(8)	3.9
S(38)	0.1434(6)	0.2203(7)	0.3948(7)	3.4
S(39)	−0.0228(6)	0.1504(7)	0.4109(7)	3.2
S(40)	−0.1662(6)	0.0834(7)	0.4051(7)	2.9
S(41)	−0.2068(6)	0.2510(7)	0.6032(7)	3.1
S(42)	−0.0594(6)	0.3114(7)	0.5712(7)	3.3
S(43)	0.1012(5)	0.3770(7)	0.5598(8)	2.8
S(44)	0.2508(6)	0.4199(7)	0.5590(7)	3.3
S(45)	0.2489(6)	0.5230(7)	0.3802(7)	3.5
S(46)	0.0987(6)	0.4610(7)	0.4087(7)	2.8
S(47)	−0.0637(6)	0.3962(7)	0.4235(7)	2.8
S(48)	−0.2116(6)	0.3499(7)	0.4228(7)	3.0
C(1)	0.332(2)	0.100(2)	0.082(2)	2.7
C(2)	0.325(2)	0.099(2)	0.181(2)	2.2
C(3)	0.200(2)	0.018(2)	0.108(2)	1.6
C(4)	0.188(2)	0.060(2)	0.179(2)	2.4
C(5)	0.068(2)	0.002(2)	0.149(2)	1.4
C(6)	−0.004(2)	−0.029(2)	0.161(2)	2.2
C(7)	−0.117(2)	−0.093(2)	0.128(2)	2.7
C(8)	−0.136(2)	−0.057(2)	0.205(2)	2.0
C(9)	−0.256(2)	−0.133(2)	0.131(3)	3.8
C(10)	−0.261(2)	−0.139(3)	0.224(3)	4.7
C(11)	0.291(2)	0.297(2)	0.135(2)	2.1
C(12)	0.277(2)	0.371(2)	0.177(3)	3.7
C(13)	0.153(2)	0.285(2)	0.129(3)	3.1
C(14)	0.136(2)	0.318(2)	0.205(3)	2.9
C(15)	0.020(2)	0.253(2)	0.182(2)	2.4
C(16)	−0.051(2)	0.228(2)	0.190(3)	3.1
C(17)	−0.168(2)	0.161(2)	0.162(3)	3.3
C(18)	−0.180(2)	0.202(2)	0.237(3)	2.7
C(19)	−0.312(2)	0.106(3)	0.175(3)	5.3
C(20)	−0.314(3)	0.127(3)	0.257(3)	6.3
C(21)	0.239(2)	0.595(3)	0.188(3)	4.6
C(22)	0.252(2)	0.589(3)	0.102(3)	4.7
C(23)	0.105(2)	0.556(2)	0.195(3)	3.4
C(24)	0.116(2)	0.515(2)	0.128(2)	2.3
C(25)	−0.015(2)	0.479(2)	0.174(2)	2.7
C(26)	−0.086(2)	0.454(2)	0.183(2)	2.3
C(27)	−0.218(2)	0.424(2)	0.229(2)	3.3
C(28)	−0.200(2)	0.389(2)	0.159(2)	2.4
C(29)	−0.357(3)	0.395(3)	0.215(3)	5.6
C(30)	−0.334(3)	0.370(3)	0.144(3)	6.2
C(31)	0.372(3)	0.896(3)	0.172(3)	6.0
C(32)	0.370(3)	0.809(3)	0.129(3)	5.5
C(33)	0.221(2)	0.839(2)	0.178(2)	2.4
C(34)	0.237(2)	0.808(2)	0.102(2)	2.4
C(35)	0.101(2)	0.783(2)	0.149(2)	1.2
C(36)	0.033(2)	0.752(2)	0.157(2)	1.9
C(37)	−0.098(2)	0.707(2)	0.211(2)	2.0
C(38)	−0.080(2)	0.679(2)	0.133(2)	2.4
C(39)	−0.236(2)	0.640(2)	0.230(3)	4.1
C(40)	−0.222(2)	0.646(2)	0.139(3)	3.4
C(41)	−0.236(2)	0.028(2)	0.562(3)	3.2
C(42)	−0.238(2)	0.016(3)	0.472(3)	4.4
C(43)	−0.093(2)	0.071(2)	0.540(2)	2.6
C(44)	−0.095(2)	0.095(2)	0.460(3)	2.8
C(45)	0.027(2)	0.140(2)	0.485(2)	1.4
C(46)	0.088(2)	0.170(2)	0.482(2)	2.6
C(47)	0.221(2)	0.201(2)	0.507(2)	1.7
C(48)	0.222(2)	0.227(2)	0.431(2)	2.1
C(49)	0.362(2)	0.217(3)	0.494(3)	4.7
C(50)	0.365(3)	0.245(3)	0.420(3)	6.6
C(51)	−0.265(2)	0.232(2)	0.532(3)	3.6
C(52)	−0.289(2)	0.299(2)	0.498(3)	3.3
C(53)	−0.139(2)	0.311(2)	0.545(2)	1.9
C(54)	−0.141(2)	0.350(2)	0.476(2)	2.6
C(55)	−0.014(2)	0.372(2)	0.494(3)	3.4
C(56)	0.053(2)	0.403(2)	0.489(2)	1.0
C(57)	0.182(2)	0.427(2)	0.512(3)	3.2
C(58)	0.177(2)	0.469(2)	0.445(2)	2.2
C(59)	0.322(2)	0.488(2)	0.504(2)	1.6
C(60)	0.322(2)	0.485(2)	0.407(2)	0.7
Cl	0.526(1)	0.0458(9)	0.109(1)	11.2

Table 1. (*continued*)

Atom	x	y	z	B_{eq}/Å^2
C(61)	0.511(1)	0.135(1)	0.145(1)	7.1
C(62)	0.504(1)	0.152(1)	0.230(1)	5.6
C(63)	0.488(1)	0.224(1)	0.259(1)	7.2
C(64)	0.480(1)	0.279(1)	0.204(1)	2.5
C(65)	0.487(1)	0.262(1)	0.120(1)	7.3
C(66)	0.503(1)	0.190(1)	0.091(1)	4.1
O	0.469(2)	0.619(2)	0.587(2)	5.2
C(67)	0.482(3)	0.603(3)	0.505(3)	5.9
C(68)	0.500(2)	0.542(3)	0.448(3)	5.3
C(69)	0.477(3)	0.668(3)	0.445(3)	7.7

Note. $B_{eq} = 4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}bc \cdot \cos\alpha + B_{13}ac \cdot \cos\beta + B_{23}ab \cdot \cos\gamma)$.

In the cationic layers, six crystallographically independent ET radical cations (denoted by A, B, C, D, E, and F in Figs. 1 and 2) are packed in stacks of two types consisting of A, B, C, and D cations and E and F cations, respectively (Fig. 3). The stacks alternate along the *c* axis in a new previously unknown sequence: two stacks of the first type, one stack of the second type, then two stacks of the first type, one stack of the second type, *etc.* Two stacks of the first type differ only in the inverted sequence of cations: ABCD...ABCD... in one of the stacks and DCBA...DCBA... in the other. In the stacks of the second type, the inversion of the cation sequence occurs after each pair of cations: EF...FE... EF...FE.... The packing mode of ET radical cations in an organic layer found in the structure of **1** exhibits fragments of known α- (see Ref. 15), α′- (see Ref. 16), and α″- (see Ref. 17) types; however, as far as we know,

Table 2. Interatomic distances (*d*) in the $[Pb_3Br_9 \cdot PhCl \cdot Me_2CO]^{3-}$ anion

Distance	d/Å	Distance	d/Å
Pb(1)—Br(1) (2)	2.976(5)	Pb(1)—Br(2) (2)	3.047(6)
Pb(1)—Br(3) (2)	3.081(5)	Pb(2)—Br(1)	2.959(6)
Pb(2)—Br(2)	3.108(7)	Pb(2)—Br(3)	3.083(7)
Pb(2)—Br(4)	3.061(7)	Pb(2)—Br(5)	2.980(6)
Pb(2)—Br(6)	3.101(6)	Pb(3)—Br(4)	3.097(6)
Pb(3)—Br(5)	3.091(6)	Pb(3)—Br(6)	2.967(6)
Pb(3)—Br(7)	3.112(6)	Pb(3)—Br(8)	2.957(7)
Pb(3)—Br(9)	3.040(6)	Pb(4)—Br(7) (2)	2.997(6)
Pb(4)—Br(8) (2)	3.000(6)	Pb(4)—Br(9) (2)	3.077(6)
Cl—C(61)	1.69(2)	C(61)—C(62)	1.40(3)
C(61)—C(66)	1.39(3)	C(62)—C(63)	1.39(3)
C(63)—C(64)	1.40(3)	C(64)—C(65)	1.39(3)
C(65)—C(66)	1.39(3)	O—C(67)	1.35(6)
C(67)—C(68)	1.43(7)	C(67)—C(69)	1.56(7)

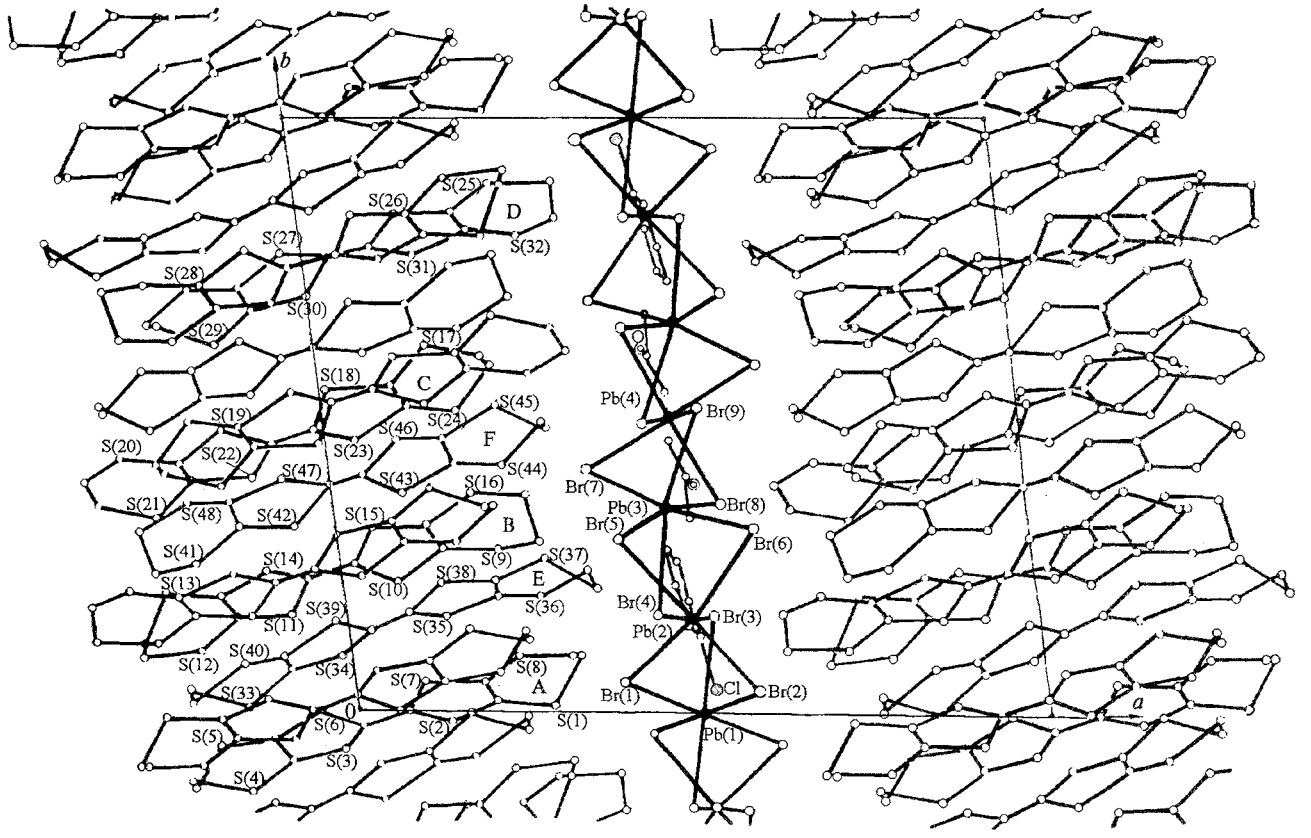


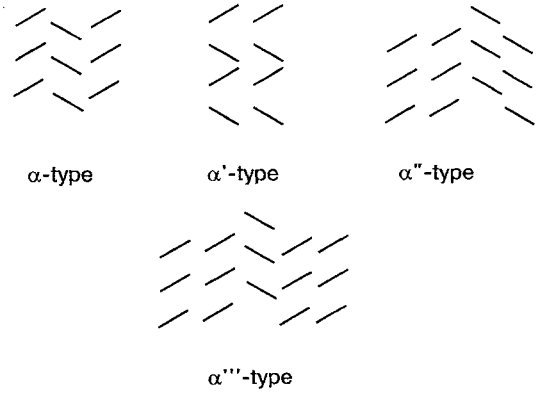
Fig. 1. Projection of the crystal structure of $(ET)_6[Pb_3Br_9PhClMe_2CO]$ onto the *ab* plane.

Table 3. Bond angles (ω) in the $[Pb_3Br_9 \cdot PhCl \cdot Me_2CO]^{3-}$ anion

Angle	ω/deg	Angle	ω/deg
Br(1)—Pb(1)—Br(2)	83.1(2)	Br(1)—Pb(1)—Br(3)	84.2(2)
Br(2)—Pb(1)—Br(3)	79.4(2)	Br(1)—Pb(2)—Br(2)	82.3(2)
Br(1)—Pb(2)—Br(3)	84.5(2)	Br(1)—Pb(2)—Br(4)	93.5(2)
Br(1)—Pb(2)—Br(5)	93.2(2)	Br(1)—Pb(2)—Br(6)	175.1(2)
Br(2)—Pb(2)—Br(3)	78.5(2)	Br(2)—Pb(2)—Br(4)	101.4(2)
Br(2)—Pb(2)—Br(5)	175.3(2)	Br(2)—Pb(2)—Br(6)	102.6(2)
Br(3)—Pb(2)—Br(4)	178.0(2)	Br(3)—Pb(2)—Br(5)	99.9(2)
Br(3)—Pb(2)—Br(6)	97.2(2)	Br(4)—Pb(2)—Br(5)	80.0(2)
Br(4)—Pb(2)—Br(6)	84.7(2)	Br(5)—Pb(2)—Br(6)	82.0(2)
Br(4)—Pb(3)—Br(5)	77.8(2)	Br(4)—Pb(3)—Br(6)	86.4(2)
Br(4)—Pb(3)—Br(7)	103.4(2)	Br(4)—Pb(3)—Br(8)	89.7(2)
Br(4)—Pb(3)—Br(9)	170.6(2)	Br(5)—Pb(3)—Br(6)	82.3(2)
Br(5)—Pb(3)—Br(7)	101.2(2)	Br(5)—Pb(3)—Br(8)	167.0(2)
Br(5)—Pb(3)—Br(9)	110.1(2)	Br(6)—Pb(3)—Br(7)	170.1(2)
Br(6)—Pb(3)—Br(8)	93.9(2)	Br(6)—Pb(3)—Br(9)	89.6(2)
Br(7)—Pb(3)—Br(8)	84.7(2)	Br(7)—Pb(3)—Br(9)	80.5(2)
Br(8)—Pb(3)—Br(9)	82.2(2)	Br(7)—Pb(4)—Br(8)	86.0(2)
Br(7)—Pb(4)—Br(9)	81.8(2)	Br(8)—Pb(4)—Br(9)	80.8(2)
Pb(1)—Br(1)—Pb(2)	83.8(2)	Pb(1)—Br(2)—Pb(2)	80.2(2)
Pb(1)—Br(3)—Pb(2)	80.0(2)	Pb(2)—Br(4)—Pb(3)	80.2(2)
Pb(2)—Br(5)—Pb(3)	81.6(1)	Pb(2)—Br(6)—Pb(3)	81.6(1)
Pb(3)—Br(7)—Pb(4)	79.8(1)	Pb(3)—Br(8)—Pb(4)	82.2(2)
Pb(3)—Br(9)—Pb(4)	79.7(2)	Cl—C(61)—C(62)	121(2)
Cl—C(61)—C(66)	119(2)	C(61)—C(62)—C(63)	120(2)
C(62)—C(61)—C(66)	120(2)	C(62)—C(63)—C(64)	120(2)
C(63)—C(64)—C(65)	120(2)	C(64)—C(65)—C(66)	120(2)
C(61)—C(66)—C(65)	120(2)	O—C(67)—C(68)	142(5)
O—C(67)—C(69)	117(4)	C(68)—C(67)—C(69)	101(4)

this packing mode as a whole was not reported in the literature. Therefore, according to the accepted notation, we consider it reasonable to call this α‴-type packing (Scheme 1).

Scheme 1



The principal geometric characteristics of the α‴ packing in the structure of **1** are given in Table 4. The dihedral angles between the mean planes of radical cations A, B, C, and D in the stacks of the first type range from 2.9 to 6.7°, while in the stacks of the second

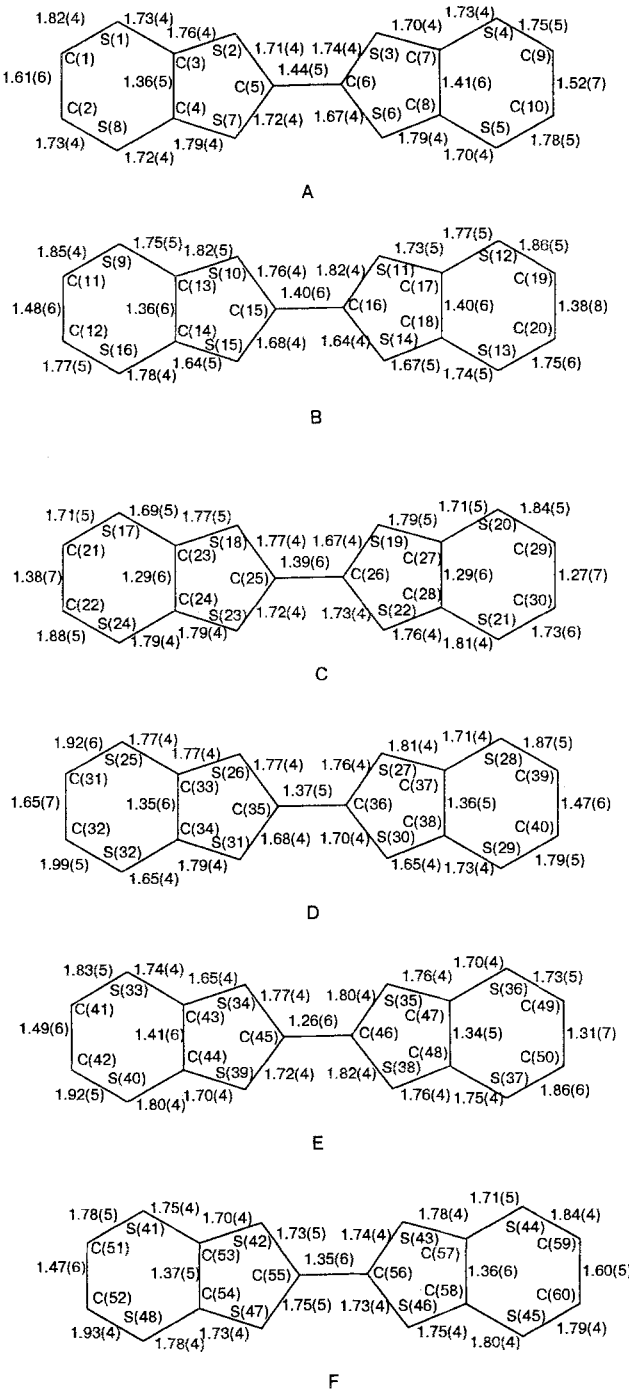


Fig. 2. Bond lengths (Å) in ET radical cations in the structure of $(ET)_6[Pb_3Br_9PhClMe_2CO]$.

type, the angles between the E/E′ and F/F′ planes related by centers of symmetry are equal to zero, and the angles between the planes of E and F cations are equal to 10.3°. The angles between the planes of cations belonging to the stacks of the first and second types are 48.2—64.8°. Interplanar distances are in the range 3.68—3.96 Å in the stacks of the first type and 3.57—3.71 Å in the stacks of the second type. Apparently, rather large

Table 4. Dihedral angles (τ) and distances (l) between the mean planes of radical cations A, B, C, D, E, and F in the structure of **1**

Radical cation	τ/deg [l/Å]					
	A	B	C	D	E	F
A	0	2.9	5.7	4.5	49.5	59.6
B	[3.96]	0	3.0	4.0	52.1	62.2
C		[3.70]	0	6.7	54.6	64.8
D			[3.68]	0	48.2	58.5
E					[3.71]	10.4
F					[3.71]	[3.57]

interplanar distances and only partial overlapping of cations in stacks (Fig. 4) account for the absence of S...S intermolecular interactions in the stacks of both types. However, these S...S interactions are observed in the cations belonging to adjacent stacks. The directions of these interactions are shown in Fig. 3; the values of shortened S...S contacts are given in Table 5.

A rather low accuracy of the determination of bond lengths in ET radical cations (see Fig. 2) results from the insufficient number of reflections observed and by the presence of heavy atoms, Pb and Br, in the structure. This prevents estimation of the charges of cations A, B, C, D, E, and F from the typical distribution of bond lengths in their TTF fragments, as accepted in the literature. The ET cations are nonplanar. Scheme 2 shows the deviations of the ethylene C atoms from the mean planes of ET. According to this scheme, ET

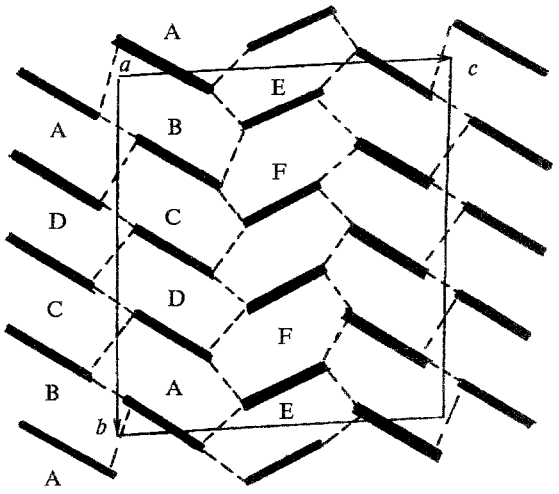


Fig. 3. Packing of ET radical cations in the conducting organic layer in the crystal structure of $(ET)_6[Pb_3Br_9PhClMe_2CO]$. The intermolecular S...S bonds are shown by dashed lines.

cations in the structure have conformations of three types: eclipsed (A), staggered (F), and intermediate (B, C, D, and E).

The anionic layer in the structure of **1** (Fig. 5) consists of $[Pb_3Br_9^{3-}]_n$ polymeric anions and PhCl and Me_2CO solvent molecules bonded to the anions. Polymeric anions are extended parallel to the [011] direction and alternate with solvent molecules along the [01$\bar{1}$] direction.

Table 5. Shortened intermolecular contacts (see Ref. 18) Br...S (<3.81 Å), Br...C (<3.68 Å), and S...S (<3.68 Å) in the structure of **1**

Contact	d/Å	Contact	d/Å
Br(1)...S(5)	3.61(1)	S(6)...S(40)	3.53(2)
Br(1)...C(10)	3.62(5)	S(7)...S(33) (−x, −y, 1+z)	3.59(2)
Br(2)...C(31)	3.56(5)	S(8)...S(33) (−x, −y, 1+z)	3.45(2)
Br(2)...C(41)	3.47(4)	S(8)...S(37)	3.49(2)
Br(3)...C(69)	3.11(5)	S(8)...S(38)	3.64(2)
Br(4)...C(32)	3.56(5)	S(12)...S(31) (−x, 1−y, −z)	3.63(2)
Br(5)...S(36)	3.62(1)	S(13)...S(48)	3.43(2)
Br(5)...C(49)	3.57(5)	S(13)...S(40)	3.67(2)
Br(5)...C(69)	2.82(6)	S(14)...S(48)	3.51(2)
Br(6)...C(10)	3.61(1)	S(14)...S(40)	3.62(2)
Br(6)...C(52)	3.57(4)	S(16)...S(37)	3.59(2)
Br(6)...C(69)	3.19(6)	S(16)...S(38)	3.54(2)
Br(7)...S(9)	3.67(1)	S(16)...S(45)	3.47(2)
Br(7)...C(11)	3.66(4)	S(16)...S(46)	3.43(2)
Br(7)...C(40)	3.61(4)	S(19)...S(48)	3.44(2)
Br(8)...C(22)	3.60(5)	S(20)...S(48)	3.50(2)
Br(8)...C(32)	3.47(5)	S(21)...S(31) (−x, 1−y, −z)	3.59(2)
Br(8)...C(65)	3.14(2)	S(21)...S(32)	3.46(2)
S(1)...S(12) (−x, −y, −z)	3.48(2)	S(23)...S(29) (−x, 1−y, −z)	3.53(2)
S(2)...S(4) (−x, −y, −z)	3.63(2)	S(24)...S(29) (−x, 1−y, −z)	3.48(2)
S(2)...S(12) (−x, −y, −z)	3.53(2)	S(25)...S(41) (−x, 1−y, 1−z)	3.58(2)
S(4)...S(9) (−x, −y, −z)	3.35(2)	S(28)...S(35) (1−x, 1−y, 1−z)	3.51(2)
S(4)...S(10) (−x, −y, −z)	3.44(2)	S(28)...S(36) (1−x, 1−y, 1−z)	3.61(2)
S(5)...S(36) (−x, −y, −z)	3.59(2)	S(28)...S(43) (1−x, 1−y, 1−z)	3.60(2)
S(5)...S(40)	3.47(2)	S(28)...S(44) (−x, 1−y, 1−z)	3.64(2)

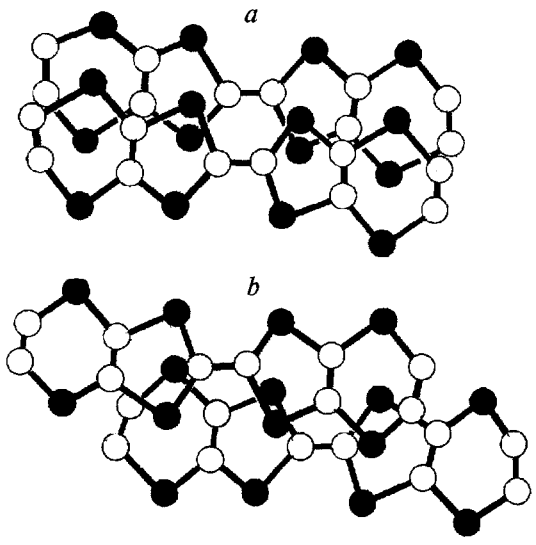


Fig. 4. Modes of overlapping of the adjacent radical cations: (*a*) A and B, B and C, D and A, E and F, F and F′; (*b*) C and D, E and E′.

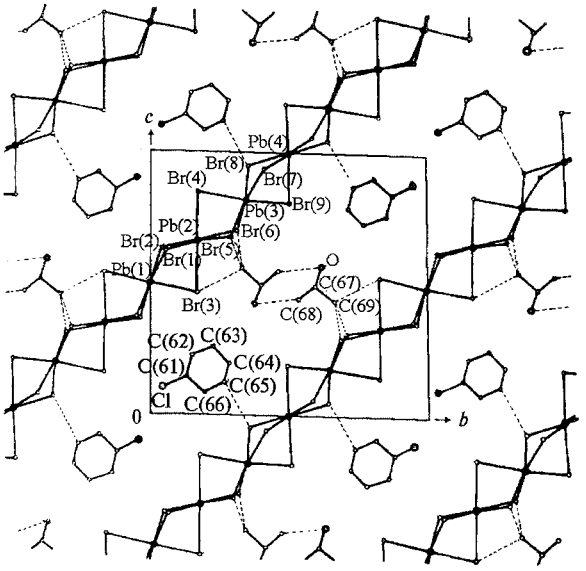


Fig. 5. Anionic layer in the crystal of **1**. Intermolecular contacts are shown by dashed lines.

The monomer unit of the polymeric anion consists of four crystallographically independent Pb atoms (two of them occupy special positions with a multiplicity of 0.5; therefore, there are three Pb atoms per unit cell) and nine Br atoms. The monomer unit has the Pb_3Br_9 composition. The bonds with Pb atoms in $[Pb_3Br_9^{3-}]_n$ polymeric anions have a distorted octahedral configuration. The Pb(1) and Pb(4) atoms occupy the centers of symmetry, which determins the crystallographic $\bar{1}$ symmetry of $Pb(1)Br_6$ and $Pb(4)Br_6$ octahedra. In the anionic polymer chain, adjacent octahedra are linked together by shared edges. Therefore, all Br atoms are bridging. The Pb—Br bond lengths and Br—Pb—Br bond angles are in the range 2.957(7)—3.112(6) Å and 77.8(2)—110.1(2)°, respectively (see Tables 2 and 3). The Pb—Pb interatomic distances in anion **1** are 3.964(2) Å [Pb(1)—Pb(2)], 3.966(3) Å [Pb(2)—Pb(3)], and 3.918(2) Å [Pb(3)—Pb(4)], *i.e.*, these distances are ~0.5 Å larger than in metallic Pb.[19]

Scheme 2

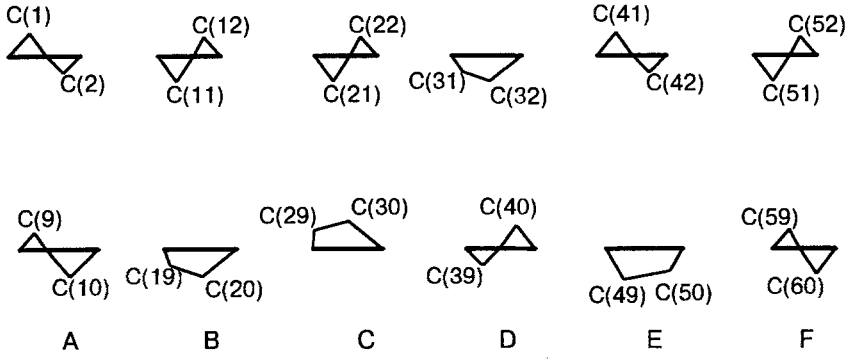


Table 6. Parameters of intermolecular hydrogen bonds in the structure of **1**

Hydrogen bond	Distance	*d*/Å	Angle	ω/deg
C(69)—H...Br(3′)	C(69)...Br(3′)	3.11(5)	C(67)—C(69)—Br(3′)	114(3)
C(69)—H...Br(5′)	C(69)...Br(5′)	2.82(6)	C(67)—C(69)—Br(5′)	117(3)
C(69)—H...Br(6′)	C(69)...Br(6′)	3.19(6)	C(67)—C(69)—Br(6′)	137(3)
C(65)—H...Br(8′)	C(65)...Br(8′)	3.14(2)	C(64)—C(65)—Br(8′)	132(1)
			C(66)—C(65)—Br(8′)	96(1)
C(68)—H...O′	C(68)...O′	2.63(6)	C(67)—C(68)—O′	151(4)

In the anionic layer, the $[Pb_3Br_9^{3-}]_n$ polymer chains are linked together in the [01$\bar{1}$] direction by bridging dimeric associates of acetone *via* intermolecular Br...H—C hydrogen bonds (Table 6). Apparently, three hydrogen bonds involving the anion favor the orientational ordering of acetone molecules in the structure of **1**, unlike a number of other crystal structures, *e.g.*, $ReCl(H_2)(PMePh_2)_4 \cdot 0.5Me_2CO$ (see Ref. 20) and β-$Mo_2Cl_4P_4C_{54}H_{52} \cdot 1.5Me_2CO$ (see Ref. 21), in which acetone solvate molecules are disordered. Besides, the $[Pb_3Br_9^{3-}]_n$ polymer chains form strong Br...H—C hydrogen bonds with chlorobenzene molecules (see Table 6).

The crystal structure of **1** exhibits a great number of shortened contacts Br...S [3.61(1)—3.67(1) Å] and Br...C [3.47(4)—3.69(5) Å] between cationic and anionic layers (see Table 5).

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