several short intramolecular non-bonded contacts in the coordination sphere,[*] the shortest being three C$\cdots$C contacts between C13 and C19 3·16 (3), C2 and C26 3·18 (2) and C18 and C19 3·18 (3) Å.

The U—I bond length of 3·041 (1) Å is not much shorter than the sum of the ionic radii of U^{4+} and $I^- = 3{\cdot}16$ Å and is to be compared with the U—I (bridging) distances 3·08 (2) and 3·11 (2) Å and the U—I (terminal) distances 2·92 (2) Å in UI_4 (Levy, Taylor, & Waugh, 1980).

The U—C distances reported in Table 2 show that the closest approaches are, in each case, to the three non-bridging atoms of the five-membered rings. The lengthening of the U—C distances to the bridging C atoms in comparison with the U—C bond lengths to the non-bridging C atoms cannot be ascribed solely to steric factors, since short intramolecular contacts involve both the non-bridging C atoms and the bridging ones. It results also from electronic factors, the negative charge of the indenyl anion residing primarily on the non-bridging C atoms. These observations confirm the conclusions reported for $U(C_9H_7)_3Cl$ (Burns & Laubereau, 1971) and for $U(C_9H_7)_3Br$ (Spirlet, Rebizant & Goffart, 1987) suggesting trihapto actinide—C π bonding with the indenyl ligands.

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[*] See deposition footnote.

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Structure of 3,4-Ethylenedithio-3′,4′-propylenedithio-2,2′,5,5′-tetrathiafulvalenium Tetraiodoindate(III)

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Abstract. 4,5-Ethylenedithio-4′,5′-trimethylenedithio-2,2′-bi-1,3-dithiolylidenium tetraiodoindate(III), $C_{11}H_{10}S_8^+.InI_4^-$, $M_r = 121{\cdot}1$, monoclinic, $P2_1/c$, $a = 6{\cdot}920\,(2)$, $b = 12{\cdot}176\,(5)$, $c = 30{\cdot}421\,(8)$ Å, $\beta = 92{\cdot}17\,(2)°$, $V = 2561\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}648$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 6{\cdot}309$ mm^{-1}, $F(000) = 1860$, $T = 296$ K. The first crystal-structure determination of a cation-radical salt containing the new unsymmetrical donor 3,4-ethylenedithio-3′,4′-propylenedithio-2,5,2′,5′-tetrathiafulvalene (EPT) is reported. The electrocrystallization of EPT with $[N(C_4H_9)_4][InI_4]$ yields a charge-transfer salt in which EPT cations and InI_4^- anions are present in a 1:1 ratio. The structure consists of dimerized stacks of EPT donor cations segregated by InI_4^- anions, forming one-dimensional chains of EPT cations oriented along the *a*-axis direction. Within each dimeric unit the EPT donors are separated by a distance of 3·29 (2) Å. Side-by-side intermolecular S$\cdots$S contacts between individual EPT donors range from 3·522 (3) to 3·688 (4) Å, the shortest of which involve the S atoms of the six- and seven-atom ethylene and propylene rings. Convergence to conventional R values of $R = 0{\cdot}080$ and $wR = 0{\cdot}044$ was obtained using 238 variable parameters and 4512 averaged reflections ($R_{\text{int}} = 0{\cdot}031$).

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Introduction. The ability of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and other derivatives of tetrathia- or tetraselenafulvalene to form conducting charge-transfer salts has stimulated considerable interest in this unusual class of compounds. The crystal structures and electrical-conduction properties of a large number of BEDT-TTF salts have been examined, several of which have been shown to be ambient-pressure superconductors (Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn, Schultz & Whangbo, 1987). Because of the ease with which the organic donor molecule can be altered synthetically, these materials offer considerable promise as a source of new electronic materials. As part of an on-going effort aimed at establishing structure–property correlations in tetrathiafulvalene-based cation-radical salts, we recently began a systematic preparation of cation-radical derivatives containing 3,4-ethylenedithio-3′,4′-propylenedithio-2,2′,5,5′-tetrathiafulvalene (EPT), an unsymmetrical derivative of BEDT-TTF. In this paper we report the X-ray crystal structure of EPT[$\mathrm{InI_4}$], an EPT salt containing a tetrahedral anion.

Experimental. EPT was prepared by a method that has been previously described (Kini, Tytko, Hunt & Williams, 1987). Black multifaceted crystals of EPT[$\mathrm{InI_4}$] obtained by electrocrystallization of EPT at a constant current of 1·1 μA cm^{-2} in 1,1,2-trichloroethane using H-cells equipped with Pt electrodes and [$\mathrm{N(C_4H_9)_4}$][$\mathrm{InI_4}$] as the supporting electrolyte. Crystal selected for data collection mounted on the (011) face with an approximate radius of 0·016 cm bounded by the faces (001), $(00\bar{1})$, (111), $(\bar{1}\bar{1}\bar{1})$, (011), $(0\bar{1}\bar{1})$, $(10\bar{1})$, $(\bar{1}01)$, (112), $(\bar{1}\bar{1}\bar{2})$. Monoclinic symmetry suggested on the basis of interaxial angles and confirmed by axial rotation photographs. Refined cell parameters obtained from the setting angles of 25 reflections with $20 < 2\theta < 25°$. ω-scan data collection carried out at ambient temperature using a Nicolet $P3/F$ diffractometer and monochromated Mo $K\alpha$ radiation [$(\sin\theta)/\lambda_{\max} =$ 0·595 Å^{-1}]. Scan rate, variable, 1–10° min^{-1}; scan range 1·8° in ω. 9094 reflections (+8, ±14, ±36) measured and averaged to give 4512 unique allowed reflections (wR_{int} = 0·031). Three standards ($10\bar{2}$, 210, $04\bar{5}$) measured every 97 data showed no significant variation over the period of data collection. The data were corrected for absorption, Lorentz and polarization effects. Absorption corrections applied using a Gaussian quadrature procedure following assignment of indices to crystal faces and careful measurement of crystal dimensions. Minimum and maximum transmission 0·392 and 0·684, respectively. Structure solution and refinement carried out using the UCLA collection of crystallographic software (Strouse, 1986). Coordinates of anion atoms obtained using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); remaining non-H atoms from difference-Fourier maps. H atoms associated with EPT donor placed in idealized positions with fixed isotropic thermal parameters. All non-H atoms refined anisotropically using full-matrix least-squares refinement. Refinement based on F_o with weights of the form $w^{-1} = \sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2]^{1/2}/(2F_o)$. Neutral atomic scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional R values of R = 0·080 and wR = 0·044 was obtained using 217 variable parameters and 4512 reflections. For final cycle, $(\Delta/\sigma)_{\max}$ = 0·05 with maximum residual electron densities of +2·05 e Å^{-3} in the vicinities of the anion I atoms.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for EPT*[$\mathrm{InI_4}$]

	x	y	z	U_{eq}*(Å^2 × 10^4)
I1	0·55446 (9)	0·12441 (6)	0·43813 (2)	528 (2)
I2	1·04262 (9)	0·18301 (7)	0·35540 (2)	665 (3)
I3	0·52910 (11)	0·37821 (6)	0·32834 (3)	661 (3)
I4	0·52166 (11)	0·02236 (6)	0·29784 (2)	622 (3)
In	0·65264 (9)	0·17727 (6)	0·35496 (2)	407 (2)
S1	0·7098 (3)	0·1056 (2)	0·99931 (8)	419 (8)
S2	1·0878 (3)	0·1840 (2)	0·97426 (8)	410 (7)
S3	0·7228 (3)	−0·0778 (2)	0·92111 (7)	390 (7)
S4	1·0961 (3)	0·0079 (2)	0·89699 (8)	455 (8)
S5	0·6530 (3)	0·2696 (2)	1·06740 (9)	532 (9)
S6	1·1118 (3)	0·3648 (2)	1·03788 (8)	452 (8)
S7	0·7174 (3)	−0·2597 (2)	0·85563 (7)	422 (8)
S8	1·1598 (4)	−0·1545 (2)	0·82725 (8)	537 (9)
C1	0·9035 (11)	0·0903 (7)	0·9656 (3)	362 (29)
C2	0·9083 (11)	0·0136 7)	0·9326 (3)	350 (28)
C3	0·8048 (11)	0·2176 (7)	1·0281 (3)	354 (28)
C4	0·9809 (11)	0·2542 (7)	1·0164 (3)	337 (28)
C5	0·8376 (12)	−0·1455 (7)	0·8788 (3)	351 (28)
C6	1·0093 (12)	−0·1056 (7)	0·8678 (3)	405 (31)
C7	0·8007 (14)	0·3782 (8)	1·0922 (3)	516 (35)
C8	0·9166 (15)	0·4435 (8)	1·0604 (3)	531 (36)
C9	0·6803 (14)	−0·2175 (8)	0·7984 (3)	506 (35)
C10	0·852 (2)	−0·2313 (9)	0·7702 (3)	603 (39)
C11	1·007 (2)	−0·1428 (10)	0·7771 (3)	714 (45)

* $U_{\mathrm{eq}} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Discussion. Atomic positional and equivalent isotropic thermal parameters for non-H atoms in this structure are given in Table 1,* with pertinent bond angles and distances summarized in Table 2. A view of the structure illustrating the atomic numbering scheme is given in Fig. 1. A stereoview packing diagram projected down the crystallographic a axis is presented in Fig. 2.

The electrocrystallization of EPT in the presence of the tetrabutylammonium salt of $\mathrm{InI_4^-}$ yields a product whose structure displays a new donor packing motif.

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44996 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°) *for* *EPT*[InI_4]

I1—In	2·7216 (11)	S5—C7	1·818 (10)
I2—In	2·6991 (12)	S6—C4	1·737 (9)
I3—In	2·7056 (13)	S6—C8	1·812 (9)
I4—In	2·6981 (11)	S7—C5	1·755 (9)
S1—C1	1·729 (8)	S7—C9	1·824 (9)
S1—C3	1·736 (8)	S8—C6	1·748 (9)
S2—C1	1·725 (8)	S8—C11	1·827 (11)
S2—C4	1·730 (8)	C1—C2	1·371 (11)
S3—C2	1·724 (8)	C3—C4	1·357 (11)
S3—C5	1·745 (8)	C5—C6	1·337 (11)
S4—C2	1·725 (8)	C7—C8	1·507 (13)
S4—C6	1·738 (9)	C9—C10	1·499 (13)
S5—C3	1·741 (8)	C10—C11	1·533 (15)

I4—In—I2	109·43 (3)	S3—C2—C1	123·3 (7)
I4—In—I3	110·17 (4)	S4—C2—C1	121·8 (7)
I4—In—I1	110·11 (4)	C4—C3—S1	116·9 (6)
I2—In—I3	106·42 (3)	C4—C3—S5	129·2 (7)
I2—In—I1	106·64 (3)	S1—C3—S5	113·9 (5)
I3—In—I1	113·89 (2)	C3—C4—S2	116·4 (6)
C1—S1—C3	95·6 (4)	C3—C4—S6	128·1 (7)
C1—S2—C4	96·1 (4)	S2—C4—S6	115·5 (5)
C5—S3—C2	95·6 (4)	C6—C5—S3	116·5 (7)
C2—S4—C6	95·7 (4)	C6—C5—S7	126·8 (7)
C5—S7—C9	101·9 (4)	S3—C5—S7	116·6 (5)
C4—S6—C8	99·8 (3)	C5—C6—S4	117·0 (7)
C3—S5—C7	101·9 (4)	C5—C6—S8	127·7 (7)
C6—S8—C11	102·8 (5)	S4—C6—S8	115·3 (5)
C2—C1—S2	121·7 (6)	C8—C7—S5	114·9 (7)
S1—C1—S2	115·0 (5)	C7—C8—S6	112·7 (7)
S1—C1—C2	123·2 (7)	C10—C9—S7	115·3 (7)
S3—C2—S4	114·8 (5)	C9—C10—C11	114·2 (9)
		C10—C11—S8	116·0 (7)

The EPT donors are present in the form of dimerized stacks that are segregated, to some extent, by both the size and location of the InI_4^- ions. The dimerized EPT units are linked in a side-by-side fashion with intermolecular S···S contacts that range from 3·522 (3) to 3·688 (4) Å. Within each dimerized unit the EPT molecules are separated by a distance of 3·29 (2) Å, a distance 0·3 Å less than the sum of the individual S-atom van der Waals radii. The individual EPT donor molecules in this structure consist of a nearly flat central tetrathiafulvalene fragment with both six- and seven-atom heterocyclic rings formed by the terminal ethylene and propylene groups. The C atoms of the ethylene portion are displaced sightly above and below the plane defined by the central TTF fragment, whereas those of the propylene end are folded forming a puckered seven-atom ring. Within the TTF framework short (<3·6 Å) intramolecular S···S contacts are numerous. Other structural details associated with the TTF fragment of this structure are unexceptional and will not be discussed further, except to note that the bond angles and distances reported in the structure described here are similar to those observed in the well known BEDT-TTF donor in many of its salts.

The InI_4^- anions in this structure are located between segregated stacks of EPT molecules and have tetrahedral coordination geometries. The deviation from ideal tetrahedral geometry is slight, with minimum and maximum I—In—I bond angles of 106·42 (3) and 113·89 (2)°, respectively. The In—I bond lengths observed in this structure show little variation and have an average length of 2·706 (12) Å. This value is in good agreement with the average value of 2·71 (1) Å reported for the tetrahedral InI_4^- anion in [$InI_2(Me_2SO)_4$][InI_4], as well as that observed in the anion of the mixed-valence In^I/In^{III} compound, In[InI_4] [2·714 (1) Å] (Einstein & Tuck, 1970; Kahn & Tuck, 1985). During the process of structure refinement, peaks of residual electron density of approximately 2·05 e Å^{-3} were noted within the vicinity of I2 and I3. Difference-Fourier maps showed evidence for possible alternate positions of two of the I atoms. However, a difference map based on a model from which the I atoms were removed indicated that the refined positions were the principal (at least 4/5) contributors to the electron density in these areas.

This communication represents the first report of the crystal structure of a cation-radical salt containing the

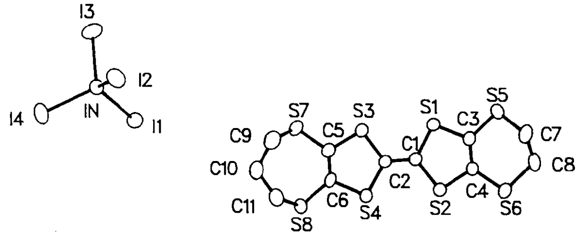

Fig. 1. A view of the EPT[InI_4] structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have been omitted for clarity.

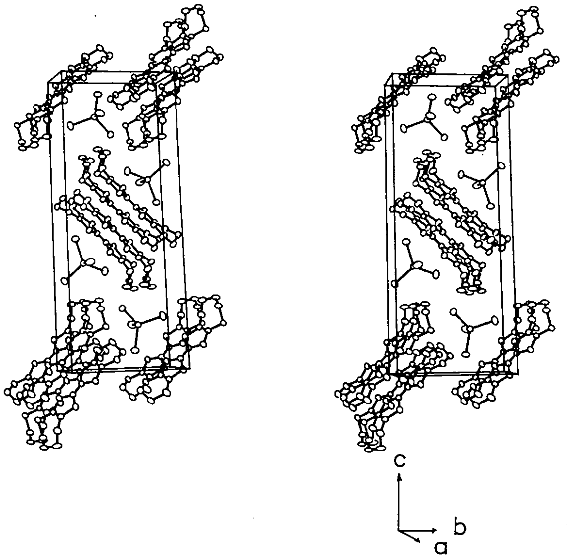

Fig. 2. A stereoview packing diagram projected down the crystallographic *a* axis.

new unsymmetrical EPT donor. The small size of the crystals obtained by electrocrystallization precluded resisitivity measurements using the four-probe technique. However, preliminary two-probe measurements indicate that the product described here is semiconducting. The dimerization of the EPT donor cations in this structure probably leads to localization of charge and, as a result, metallic conductivity is not expected.

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Structure of the Adduct Lithium Hexacyanoferrate(II)–Hexamethylenetetramine–Water (1/2/5)

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Abstract. $Li_4[Fe(CN)_6].2C_6H_{12}N_4.5H_2O$, $M_r = 610{\cdot}2$, orthorhombic, $Imm2$, $Z = 2$, $a = 14{\cdot}849\ (3)$, $b = 10{\cdot}393\ (3)$, $c = 9{\cdot}098\ (3)$ Å, $V = 1404\ (3)$ Å^3, $D_x = 1{\cdot}44$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}4$ cm^{-1}, $F(000) = 436$, room temperature, final $R = 0{\cdot}040$ for 729 unique reflections and 129 variables. The structure consists of a body-centred arrangement of $[Fe(CN)_6]^{4-}$ octahedra, $C_6H_{12}N_4$ molecules which occupy the tetrahedral interstices, and $[Li_4(OH_2)_5]^{4+}$ units, which occupy the octahedral interstices. The Li ions are further connected by Li—N contacts to the hexamethylene tetramine molecules and hexacyanoferrate groups.

Introduction. The crystal structures of addition compounds of metal hexacyanoferrates with hexamethylenetetramine (HMT) (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) investigated so far show comparable building patterns (Meyer & Pickardt, 1988). The structures may be thought of as derived from the cubic elpasolite structure: the hexacyanoferrate ions form a base lattice that is close to face-centred cubic, the tetrahedral interstices are occupied by HMT molecules, the octahedral interstices by hydrated cations. Depending on the size of the cations and the number of water molecules coordinated to the cations, distortion of the lattice occurs, and less symmetric structures result. The title compound also shows this pattern, but crystallizes in a transformed body-centred cell. The lithium hexacyanoferrate(III) compound $Li_3[Fe(CN)_6].2C_6H_{12}N_4.5H_2O$ (Pickardt, Kähler, Rautenberg & Riedel, 1984) is isostructural but possesses disordered lithium ions.

Experimental. Pale-yellow transparent crystals were obtained by diffusion of a solution of HMT in methanol into an aqueous phase containing lithium hexacyanoferrate(II). The compound was characterized by CHN analysis, C% 34·48 (calc. 35·43), H% 5·70 (5·62), N% 32·14 (32·14), and by IR spectroscopy. From Buerger precession photographs the symmetry was found to be orthorhombic, space group $Imm2$, derived from systematic absences hkl ($h+k+l = 2n+1$) and discriminated from $Immm$ *etc.* during the structure determination process. Octahedral crystal $0{\cdot}20 \times 0{\cdot}15 \times 0{\cdot}15$ mm; diffractometer Syntex $P2_1$, Mo $K\alpha$ radiation, graphite monochromator; cell parameters from 15 reflections

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