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# Europium antimony sulfide, $Eu_6Sb_6S_{17}$

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**Key indicators**

Single-crystal X-ray study
$T$ = 193 K
Mean $\sigma$(S–S) = 0.003 Å
$R$ factor = 0.031
$wR$ factor = 0.062
Data-to-parameter ratio = 26.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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$Eu_6Sb_6S_{17}$ is isotypic with $Sr_6Sb_6S_{17}$ and can be regarded as consisting of two isolated $[Sb_3S_7]^{5-}$ anions and an $S_3{}^{2-}$ polysulfide anion that are joined together by $Eu^{2+}$ cations. There are six crystallographically unique $Eu^{2+}$ cations bound by sulfide and polysulfide anions in seven-, eight- and nine-coordinate environments. Each of the $[Sb_3S_7]^{5-}$ anions consists of a trinuclear assembly of corner-sharing $SbS_3$ units. The $[Sb_3S_7]^{5-}$ anions are connected by long (3.1 Å) Sb—S interactions, forming one-dimensional ribbons running down the *a* axis and packed with opposing directions of polarity. The bent $S_3{}^{2-}$ anions stack in columns parallel to the *a* axis, oriented in opposing directions with respect to one another. The overall structure is three-dimensional and has channels running down the *a* axis to house the stereochemically active lone pair of electrons on the $Sb^{3+}$ centers. The presence of $Eu^{2+}$ is supported by both magnetic measurements and bond-valence calculations.

## Comment

Ternary rare-earth thioantimonites have been known for more than 20 years, since the initial report of the synthesis and crystal structure of $Eu_3Sb_4S_9$ (Lemoine *et al.*, 1981). Despite this early success, the chemistry of thioantimonites is relatively undeveloped compared to that of thiophosphates (Evenson & Dorhout, 2001; Kanatzidis, 1997), and there is still a dearth of understanding in the structure–property relationships in this system. There has been renewed interest in ternary and quaternary chalcoantimonites and chalcobismuthites owing to their potential applications as thermoelectric materials. Based on structural analogies with $Pn_2Q_3$ phases (Pn = Sb and Bi, and $Q$ = S, Se and Te), a series of ternary phases such as $EuSb_2Q_4$, $EuSb_2Q_7$, and $EuBi_2Te_4$ has been prepared and their transport properties measured (Godzhaev *et al.*, 1978; Harman & Honig, 1967). $EuBi_2Te_4$ displays a thermoelectric figure of merit comparable to that of $Bi_2Te_3$ (Godzhaev *et al.*, 1978; Harman & Honig, 1967). $Eu_2BiS_4$ is also of particular interest because it contains $Eu^{II}$ and $Eu^{III}$ in different coordination environments (Carré *et al.*, 1985). Other ternary rare-earth thioantimonites, such as $Pr_8Sb_2S_{15}$ (Guseinov *et al.*, 1981), $Ln_3Sb_3S_{10}$ (Ln = La and Ce; Gao *et al.*, 1983) and $Ln_6Sb_8S_{21}$ (Ln = La and Ce; Gao *et al.*, 1984), have been characterized from single-crystal and powder X-ray diffraction data. $EuSb_4S_7$ has also been reported, but only its lattice constants are known (Aliev *et al.*, 1978).

More recently, there has been attention paid to preparing quaternary rare-earth chalcoantimonites and chalcobismuthites, *e.g.* $K_2(Ln_{2-x})Sb_{4+x}Sb_4Se_{12}$ (Ln = La, Ce, Pr and Gd; Chen & Dorhout, 1997), $K_2Gd_2Sb_2Se_9$ (Choi *et al.*, 1999), $K_2La_2Sb_2S_9$ (Choi *et al.*, 1999), $Na_9Gd_5Sb_8S_{26}$ (Park & Kim,

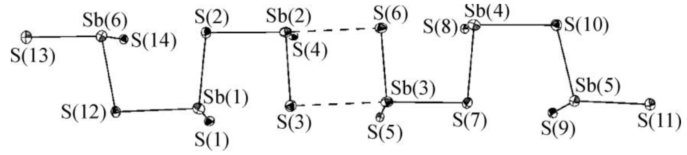

**Figure 1**
A view of the $[Sb_3S_7]^{5-}$ anions, which consist of trinuclear assemblies of corner-sharing $SbS_3$ units in $Eu_6Sb_6S_{17}$. 50% probability displacement ellipsoids are depicted.

2001), $BaLaBi_2S_6$ (Choi *et al.*, 1997), $ALn_{1\pm x}Bi_{4\pm x}S_8$ ($A$ = K and Rb, and Ln = La, Ce, Pr and Nd; Iordanidis *et al.*, 1999) and $Pb_2Eu_2Bi_6Se_{13}$ (Chung *et al.*, 1998). These compounds possess complex structures, owing to the combination of the high coordination numbers found for lanthanides with discrete $[PnQ_3]^{3-}$, $[PnQ_{3+1}]^{3-}$ and $[PnQ_4]^{5-}$ anions and the extended networks of chalcoantimonites and chalcobismuthites. We report here the preparation and crystal structure of $Eu_6Sb_6S_{17}$, a new ternary thioantimonite that is isotypic with $Sr_6Sb_6S_{17}$ (Choi & Kanatzidis, 2000) and homeotypic with $Pb_6Sb_6S_{17}$ (with one of the axes halved) (Orlandi *et al.*, 2002), and which contains $Eu^{II}$ and a polysulfide linkage.

Although three-dimensional in nature, the structure of $Eu_6Sb_6S_{17}$ can be treated as consisting of two isolated $[Sb_3S_7]^{5-}$ anions and an $S_3^{2-}$ polysulfide anion that are joined together by $Eu^{2+}$ cations. Analogous to $Sr_6Sb_6S_{17}$ (Choi & Kanatzidis, 2000), charge balance is attained in a straightforward manner by assuming the presence of six $Eu^{2+}$ cations, six $Sb^{3+}$ cations, 14 $S^{2-}$ anions and one $S_3^{2-}$ anion. The $[Sb_3S_7]^{5-}$ anion consists of a trinuclear assembly of corner-sharing $SbS_3$ units, as shown in Fig. 1. Other anions formed from the linking of $SbS_n$ units include $[Sb_2S_4]^{2-}$ in $BaSb_2S_4$ (Cordier *et al.*, 1984) and $[Sb_2S_5]^{4-}$ in $Sr_2Sb_2S_5\cdot15H_2O$ (Schwidetzky, 1985). The Sb—S bond distances range from 2.416 (2) to 2.664 (3) Å. As in $Sr_6Sb_6S_{17}$ (Choi & Kanatzidis, 2000), the $[Sb_3S_7]^{5-}$ anions are connected by long 3.105 (3) to 3.106 (3) Å Sb$\cdots$S interactions to form one-dimensional ribbons running down the *a* axis. Each of the $Sb^{3+}$ cations possesses a stereochemically active lone pair of electrons.

Although the space group $P2_12_12_1$ in which this compound crystallizes is non-centrosymmetric but non-polar, there is approximate alignment of the lone pair of electrons on the individual $Sb^{3+}$ cations parallel to the *b* axis. However, the $[Sb_3S_7]^{5-}$ anions are packed with opposing directions of polarity (*i.e.* the lone-pairs on different anions are aligned in opposite directions). The $S_3^{2-}$ anion is bent, with S—S bond distances of 2.091 (3) and 2.092 (3) Å, and an S—S—S bond angle of 113.34 (15)°. Although the polysulfide anions do stack in oriented columns parallel to the *a* axis, the columns are oriented in opposing directions with respect to one another, canceling any polarity.

The six crystallographically unique $Eu^{2+}$ cations are found in a variety of coordination environments, as shown in Fig. 2. Atoms Eu1 and Eu2 are found in seven-coordinate monocapped trigonal prismatic environments, with Eu—S bond distances ranging from 2.984 (3) to 3.081 (3) Å, and 2.944 (3) to 3.209 (3) Å, respectively. Atom Eu3 is bound by eight sulfide anions, with bond distances ranging from 2.968 (2) to 3.235 (3) Å. The geometry around atom Eu3 is heavily distorted from being a bicapped trigonal prism, a square antiprism or a dodecahedron because two of the sulfide nearest neighbors are part of the polysulfide linkage, creating a very short edge on the polyhedron. Atoms Eu4, Eu5 and Eu6 are all in nine-coordinate geometries that are quite distorted from idealized tricapped trigonal prismatic symmetry because of the presence of a polysulfide linkage within their inner spheres. The Eu4—S, Eu5—S and Eu6—S bond distances range from 3.005 (3) to 3.382 (3) Å, 2.980 (2) to 3.208 (2) Å, and 2.988 (3) to 3.197 (3) Å, respectively. Bond-valence sum calculations provide values ranging from 1.87 to 2.10 for the Eu centers in $Eu_6Sb_6S_{17}$, which are consistent with $Eu^{2+}$ in this compound (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). Measurements of the magnetic susceptibility show that the effective magnetic moment is 7.0 $\mu_B$/Eu, which is somewhat lower than the expected free-ion moment of 7.9 $\mu_B$ for $Eu^{2+}$ because of the presence of minor amounts of $Sb_2S_3$ impurities. An antiferromagnetic transition occurs at 3.2 K in the susceptibility curve. A packing diagram for the complete structure of $Eu_6Sb_6S_{17}$ is shown in Fig. 3. When the structure is viewed down the *a* axis, it becomes apparent that $Eu_6Sb_6S_{17}$ adopts a channel structure. These

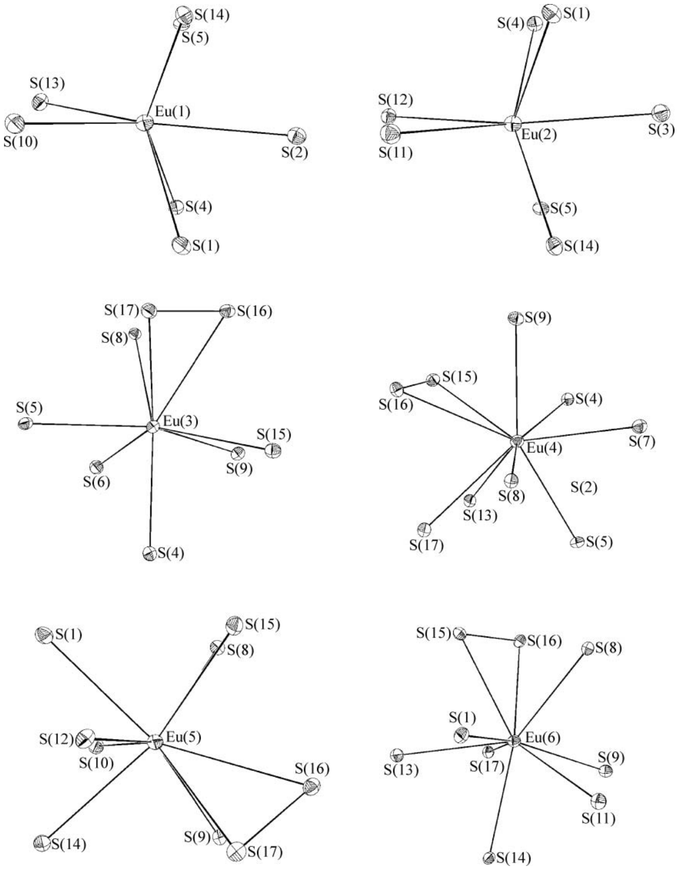

**Figure 2**
A depiction of the local environments of the six crystallographically unique $Eu^{2+}$ cations in $Eu_6Sb_6S_{17}$. 50% probability displacement ellipsoids are depicted.

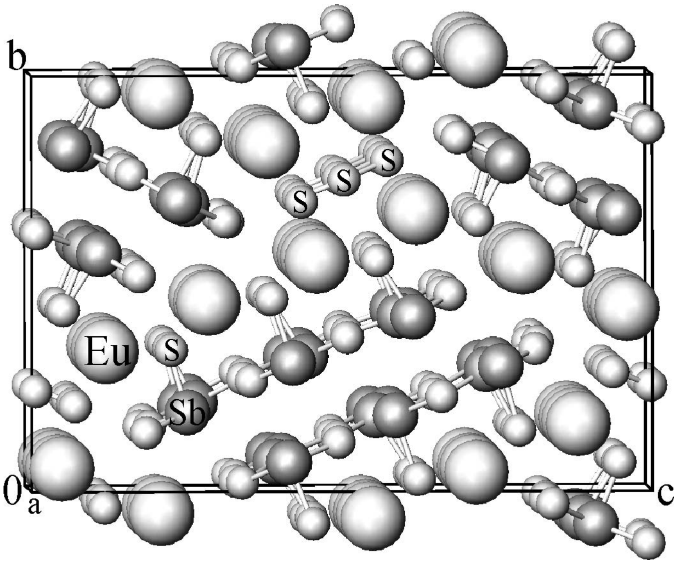

**Figure 3**
The three-dimensional channel structure of $Eu_6Sb_6S_{17}$ viewed down the *a* axis. Eu—S bonds have been omitted for clarity.

channels house the stereochemically active lone pair of electrons on the $Sb^{3+}$ centers. A similar channel motif is also observed for $Eu_3Sb_4S_9$ (Lemoine *et al.*, 1981).

## Experimental

Eu foil (99.9%, Alfa-Aesar), Sb (99.5%, Alfa-Aesar) and S (99.5%, Alfa-Aesar) were loaded in a fused-silica tube in a molar ratio of 3:5:12 with a total mass of 0.250 g. The following heating profile was used: 5 K min$^{-1}$ to 1123 K for 1 d, 5 K min$^{-1}$ to 1273 K for 7 d, 0.5 K min$^{-1}$ to 873 K for 5 d, and 0.25 K min$^{-1}$ to 295 K. The product consisted of small black block-shaped crystals of $Eu_6Sb_6S_{17}$ and acicular crystals of $Sb_2S_3$. The yields were generally low (about 10%), and were not improved by quenching the reactions. Semi-quantitative SEM/EDX analysis was performed on crystals of $Eu_6Sb_6S_{17}$ using a Jeol 840/Link Isis instrument. Eu, Sb and S percentages were calibrated against standards, and a Eu:Sb:S ratio of close to 1:1:2.8 (20 mol%:23 mol%:57 mol%) was found.

### *Crystal data*

$Eu_6Sb_6S_{17}$
$M_r = 2187.28$
Orthorhombic, $P2_12_12_1$
$a = 8.236$ (2) Å
$b = 15.237$ (3) Å
$c = 22.724$ (5) Å
$V = 2851.7$ (11) Å$^3$
$Z = 4$
$D_x = 5.095$ Mg m$^{-3}$

Mo *Kα* radiation
Cell parameters from 7062 reflections
$\theta = 1.6$–28.3°
$\mu = 19.80$ mm$^{-1}$
$T = 193$ (2) K
Prism, black
0.11 × 0.08 × 0.05 mm

### *Data collection*

Bruker SMART APEX diffractometer
$\omega$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\min} = 0.102$, $T_{\max} = 0.383$
29271 measured reflections

7062 independent reflections
6058 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\max} = 28.3°$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 19$
$l = -30 \rightarrow 30$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.062$
$S = 1.00$
7062 reflections
264 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.41$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.23$ e Å$^{-3}$
Extinction correction: *SHELXTL*
Extinction coefficient: 0.000081 (7)
Absolute structure: Flack (1983), 3084 Friedel pairs
Flack parameter: 0.699 (16)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Eu1—S5$^{\mathrm{i}}$ | 2.984 (3) | Eu5—S8 | 2.980 (2) |
| Eu1—S4 | 2.987 (3) | Eu5—S14 | 2.984 (3) |
| Eu1—S1 | 3.000 (3) | Eu5—S17$^{\mathrm{vii}}$ | 3.027 (2) |
| Eu1—S14$^{\mathrm{ii}}$ | 3.009 (3) | Eu5—S1$^{\mathrm{viii}}$ | 3.039 (3) |
| Eu1—S10$^{\mathrm{ii}}$ | 3.028 (3) | Eu5—S10 | 3.073 (3) |
| Eu1—S2 | 3.056 (3) | Eu5—S9 | 3.082 (2) |
| Eu1—S13$^{\mathrm{iii}}$ | 3.081 (3) | Eu5—S15 | 3.110 (3) |
| Eu1···Eu2$^{\mathrm{i}}$ | 4.0983 (12) | Eu5—S12 | 3.168 (3) |
| Eu1···Eu5$^{\mathrm{ii}}$ | 4.1297 (11) | Eu5—S16$^{\mathrm{vii}}$ | 3.208 (2) |
| Eu1···Eu2 | 4.1394 (12) | Eu5···Eu6 | 4.0621 (12) |
| Eu1···Eu4$^{\mathrm{i}}$ | 4.1683 (11) | Eu5···Eu1$^{\mathrm{viii}}$ | 4.1296 (11) |
| Eu2—S11$^{\mathrm{iv}}$ | 2.944 (3) | Eu6—S1$^{\mathrm{ix}}$ | 2.988 (3) |
| Eu2—S4 | 2.962 (3) | Eu6—S14 | 3.017 (3) |
| Eu2—S5 | 2.981 (2) | Eu6—S9 | 3.035 (2) |
| Eu2—S14$^{\mathrm{iv}}$ | 2.982 (3) | Eu6—S8$^{\mathrm{vi}}$ | 3.046 (2) |
| Eu2—S1 | 3.008 (3) | Eu6—S11 | 3.063 (3) |
| Eu2—S3 | 3.010 (3) | Eu6—S15$^{\mathrm{vi}}$ | 3.095 (2) |
| Eu2—S12$^{\mathrm{v}}$ | 3.209 (3) | Eu6—S17$^{\mathrm{vii}}$ | 3.101 (3) |
| Eu2···Eu1$^{\mathrm{vi}}$ | 4.0983 (12) | Eu6—S13 | 3.167 (3) |
| Eu2···Eu6$^{\mathrm{iv}}$ | 4.1127 (11) | Eu6—S16$^{\mathrm{vi}}$ | 3.197 (3) |
| Eu2···Eu3 | 4.1743 (11) | Eu6···Eu2$^{\mathrm{ix}}$ | 4.1127 (11) |
| Eu3—S9$^{\mathrm{i}}$ | 2.968 (2) | Eu6···Eu3$^{\mathrm{vi}}$ | 4.1587 (11) |
| Eu3—S5 | 3.005 (3) | Sb1—S1 | 2.449 (2) |
| Eu3—S4 | 3.015 (3) | Sb1—S2 | 2.507 (3) |
| Eu3—S6 | 3.023 (3) | Sb1—S12$^{\mathrm{ii}}$ | 2.664 (3) |
| Eu3—S8 | 3.024 (2) | Sb2—S3 | 2.426 (3) |
| Eu3—S17 | 3.051 (3) | Sb2—S4 | 2.464 (2) |
| Eu3—S15$^{\mathrm{v}}$ | 3.132 (3) | Sb2—S2 | 2.598 (3) |
| Eu3—S16 | 3.235 (3) | Sb3—S6 | 2.431 (3) |
| Eu3···Eu4 | 4.0614 (12) | Sb3—S5 | 2.471 (2) |
| Eu3···Eu6$^{\mathrm{i}}$ | 4.1587 (11) | Sb3—S7 | 2.587 (3) |
| Eu3···Eu4$^{\mathrm{i}}$ | 4.1753 (12) | Sb4—S8 | 2.416 (2) |
| Eu4—S4$^{\mathrm{vi}}$ | 3.005 (3) | Sb4—S7 | 2.537 (3) |
| Eu4—S5 | 3.009 (2) | Sb4—S10 | 2.644 (3) |
| Eu4—S8 | 3.010 (2) | Sb5—S11 | 2.436 (3) |
| Eu4—S9 | 3.044 (2) | Sb5—S9 | 2.440 (2) |
| Eu4—S15$^{\mathrm{vii}}$ | 3.066 (3) | Sb5—S10 | 2.534 (3) |
| Eu4—S7 | 3.077 (3) | Sb6—S13 | 2.434 (3) |
| Eu4—S17 | 3.098 (3) | Sb6—S14 | 2.445 (2) |
| Eu4—S16$^{\mathrm{vii}}$ | 3.157 (3) | Sb6—S12 | 2.520 (3) |
| Eu4—S13$^{\mathrm{v}}$ | 3.382 (3) | S15—S16 | 2.091 (3) |
| Eu4···Eu5 | 4.1417 (11) | S16—S17 | 2.092 (3) |
| Eu4···Eu1$^{\mathrm{vi}}$ | 4.1683 (11) | | |
| | | | |
| S1—Sb1—S2 | 91.74 (9) | S8—Sb4—S10 | 90.92 (9) |
| S1—Sb1—S12$^{\mathrm{ii}}$ | 91.51 (9) | S7—Sb4—S10 | 95.27 (9) |
| S2—Sb1—S12$^{\mathrm{ii}}$ | 96.50 (9) | S11—Sb5—S9 | 94.14 (9) |
| S3—Sb2—S4 | 96.62 (9) | S11—Sb5—S10 | 103.87 (8) |
| S3—Sb2—S2 | 93.86 (8) | S9—Sb5—S10 | 90.28 (10) |
| S4—Sb2—S2 | 93.15 (9) | S13—Sb6—S14 | 95.92 (9) |
| S6—Sb3—S5 | 94.92 (10) | S13—Sb6—S12 | 100.90 (9) |
| S6—Sb3—S7 | 94.70 (7) | S14—Sb6—S12 | 94.00 (9) |
| S5—Sb3—S7 | 92.21 (9) | S15—S16—S17 | 113.34 (15) |
| S8—Sb4—S7 | 92.32 (9) | | |

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, -y-1, z+\frac{1}{2}$; (iii) $x-\frac{3}{2}, -y-\frac{3}{2}, -z$; (iv) $-x+\frac{3}{2}, -y-1, z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y-\frac{3}{2}, -z$; (vi) $x+1, y, z$; (vii) $x+\frac{1}{2}, -y-\frac{3}{2}, -z$; (viii) $-x+\frac{1}{2}, -y-1, z-\frac{1}{2}$; (ix) $-x+\frac{3}{2}, -y-1, z-\frac{1}{2}$.

Inspection of the atomic positions reveals that they come in symmetry-related pairs (*e.g.* Eu1–Eu2, Eu3–Eu4 and Eu5–Eu6) and

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the presence of additional pseudo-symmetry elements is confirmed by *PLATON* (Spek, 2003). The structure can be refined in space group *Pmnb* (alternative setting of the standard space group *Pnma*) to a residual of $R(F) = 0.11$ if a large number of systematic absence exceptions are excluded. The structure in *Pmnb* is identical to the structure in $P2_12_12_1$, except that the $S_3^{2-}$ groups are in a disordered arrangement. We conclude, in agreement with Choi & Kanatzidis (2000), that the correct space group is indeed $P2_12_12_1$. The sole atom that breaks the mirror symmetry is S16. The crystal of $Eu_6Sb_6S_{17}$ which was examined proved to be a partial inversion twin. The highest peak and the deepest hole are located 0.98 and 1.77 Å from atoms Eu1 and S1, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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