N ($-1\cdot0$ e Å^{-3}). One other minimum was found at 0·25, 0·25, 0 ($-1\cdot4$ e Å^{-3}).

Discussion. The anion consists of six Cl atoms in a regular octahedral arrangement about a central Tc atom. The Tc—Cl bond distance is 2·3531 (5) Å. This value is in close agreement with the value of 2·35 (1) Å found previously for the analogous K salt (Elder *et al.*, 1967). It is significantly less than the value of 2·46 Å predicted from ionic radii (Shannon, 1976). Ammonium ions are known to have low barriers to rotation in many crystals [see, for example, the recent review by Hüller (1977)]. This is presumably the reason why the H atoms in this structure could not be successfully located.

All calculations were performed on an Amdahl 470/V6 computer located at the University of Cincinnati. A locally modified version of XRAY 67 (Elder, 1974) was used for all calculations. This study was supported by the National Institutes of Health (Grant No. HL-21276-01).

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Structure of Orthorhombic CeS_2 Prepared at 1773 K and 5·5 GPa

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Abstract. $Pn2_1a$, $a = 8\cdot103$ (2), $b = 16\cdot221$ (2), $c = 4\cdot093$ (1) Å, $Z = 8$ and $D_x = 5\cdot06$ Mg m^{-3}. The structure is roughly expressed as the stacking of three kinds of layers *A*, *B* and *C* parallel to (010) with layer sequence *ABCACBA*. The layer *A* consists of S ions and the layers *B* and *C* of Ce and S ions. Each Ce atom is coordinated to nine S atoms, the average Ce—S distance being 3·01 (2) Å. All S ions in the *A* layer form pairs, the bond length of the pair being 2·18 (2) Å, while the distances between unpaired S atoms are in the range 3·03 to 4·14 Å. The difference between the orthorhombic and monoclinic structures is primarily in the layer sequence.

Introduction. Cerium polysulphide, CeS_2, crystallizes in the monoclinic form with a pseudocubic symmetry (Picon & Patrie, 1956; Flahaut & Guittard, 1956; Marcon & Pascard, 1968). A polymorphic phase, which is isostructural with orthorhombic LaS_2, has been synthesized under pressure (Yanagisawa & Kume, 1973). Single crystals were grown at 1773 K and 5·5 GPa. The size of each grain was approximately 0·2 × 0·2 × 0·1 mm.

The symmetry was orthorhombic and systematic extinctions were $hk0$ with $h = 2n + 1$ and $0kl$ with $k + l = 2n + 1$, indicating that the space group was either $Pn2_1a$ or $Pnma$. A set of three-dimensional intensity data of 688 reflections to $\sin\theta/\lambda = 0\cdot75$ Å^{-1} were collected with a Rigaku Denki four-circle diffractometer using monochromated Mo $K\alpha$ radiation. The intensity data were corrected for Lorentz and polarization factors, but no absorption correction was made. The structure was solved from a Patterson map. Refinement was carried out by the block-diagonal least-squares method

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with the computer program *RSDLS*-3 (Ashida, 1973) until the maximum shift of each parameter became less than $\frac{1}{20}$ of its e.s.d. The atomic scattering factors for Ce and S were taken from *International Tables for X-ray Crystallography* (1962). R decreased to 0·084 in the case of $Pn2_1a$, while it remained at 0·35 for $Pnma$. Thus the space group was determined as $Pn2_1a$. The weighted R was 0·088 for $w = 1$ and this is the minimum of values of $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Discussion. The positional parameters and the interatomic distances are given in Tables 1 and 2 respectively.* A perspective view of the structure is shown in Fig. 1. This structure contains a set of slightly puckered layers of S(3) and S(4) atoms parallel to (010) levels close to $y = 0$ and $\frac{1}{2}$; these layers are denoted here as A layers. There are other kinds of layers at approximately $y = 0\cdot15$ and $0\cdot35$ in which both Ce and S ions are closely packed. If these layers are named B and C layers respectively, the whole structure is expressed by a repetition of the sequence of $ABCACBA$ layers.

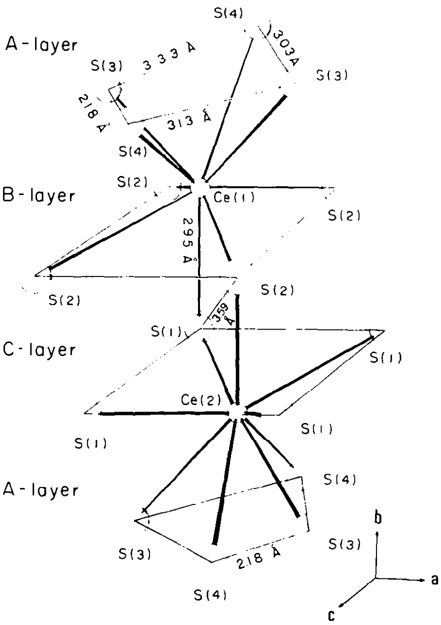

Fig. 1. A perspective view of part of the structure. The large circles represent S ions and the small circles Ce. Approximate directions of the axes are shown in the figure. The layers A, B and C are explained in the text.

The structure of monoclinic CeS_2 is of the same type as that of $CeSe_2$ (Ring & Tecotzky, 1964). The structure of $CeSe_2$ has been precisely analysed (Marcon & Pascard, 1968). If the layers are stacked in the order $ABCABCA$, the monoclinic phase is formed. In this case the crystal axes and the lattice parameters for the orthorhombic and monoclinic cells are related by $a_{\text{mono}} = a_{\text{orth}}$, $b_{\text{mono}} = c_{\text{orth}}$ and $2c_{\text{mono}} = b_{\text{orth}}$.

In both the monoclinic and orthorhombic phases, each Ce atom is coordinated to nine S atoms. All S ions in the A layer form so-called dumb-bell pairs and the S—S distance in the pair is 2·18 Å. The S ions in the B and C layers and those in neighbouring layers are separated by distances of 3·03 to 4·14 Å.

The compound LaS_{1+x} also crystallizes in an orthorhombic structure when the ratio La/S is close to $\frac{1}{2}$ (Ring & Tecotzky, 1964). Although no precise analysis of the structure of orthorhombic LaS_2 has been made, a resemblance between the X-ray powder diffraction pattern of LaS_2 and that of orthorhombic CeS_2 suggests that the atomic arrangement of LaS_2 would be similar to that of CeS_2 shown in the present work.

Table 1. *Positional parameters with estimated standard deviations in parentheses*

	x	y	z
Ce(1)	0·1272 (4)	0·1386 (2)	0·2241 (5)
Ce(2)	0·3726 (3)	0·3618 (2)	0·7302 (7)
S(1)	0·1208 (14)	0·3201 (6)	0·2465 (30)
S(2)	0·3690 (16)	0·1858 (6)	0·7433 (27)
S(3)	0·3863 (14)	0·0060 (9)	0·1469 (27)
S(4)	0·1034 (15)	0·0047 (15)	0·6649 (26)

Table 2. *Interatomic distances* (Å) *with estimated standard deviations in parentheses*

Ce(1)–Ce(1)	4·057 (5)	S(1)–S(1)	4·05 (2)
	4·489 (6)		4·09 (2)
Ce(1)–Ce(2)	4·621 (5)	S(1)–S(2)	3·59 (2)
Ce(1)–S(1)	2·95 (1)		3·64 (2)
Ce(1)–S(2)	2·99 (1)	S(1)–S(3)	3·26 (2)
	2·88 (1)		3·74 (2)
	2·94 (1)	S(1)–S(4)	3·52 (2)
	3·12 (2)		3·75 (2)
Ce(1)–S(3)	3·16 (1)	S(2)–S(2)	4·05 (2)
	3·10 (1)		4·09 (2)
Ce(1)–S(4)	2·83 (2)	S(2)–S(3)	3·53 (2)
	3·16 (2)		3·96 (2)
Ce(2)–S(1)	2·88 (1)	S(2)–S(4)	3·52 (2)
	2·99 (1)		3·53 (2)
	3·01 (1)	S(3)–S(3)	4·09 (2)
	3·02 (1)		4·14 (2)
Ce(2)–S(2)	2·89 (1)	S(3)–S(4)	2·18 (2)
Ce(2)–S(3)	3·01 (1)		3·03 (2)
	3·08 (1)		3·13 (2)
Ce(2)–S(4)	2·93 (1)		3·33 (2)
	3·28 (2)	S(4)–S(4)	4·09 (2)
			4·11 (2)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33904 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of the Bismuth Chloride Sulphide $Bi_4Cl_2S_5$

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Abstract. $Bi_4Cl_2S_5$, rhombohedral, $R\bar{3}$, a = 19·804 (5), c = 12·359 (3) Å, Z = 15, V = 4197·4 Å^3, D_c = 6·33 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 60·89 mm^{-1}, $F(000)$ = 6690. Systematic absences hkl, $-h + k + l = 3n$. Final R = 0·056. The structure has: (*a*) statistical occupancy of the anions sites by S and Cl (S + Cl = X); (*b*) unusual Bi–X coordination polyhedra. One Bi has nine X neighbours at 2·88, 2·90, and 3·44 Å; the remaining three are irregularly surrounded by eight X between 2·62 and 3·66 Å.

Introduction. Besides BiHalS (Hal: Cl, Br, I) and the halogen-poor $Bi_{19}Hal_3S_{27}$, only $Bi_4Cl_2S_5$ could be prepared (Krämer, 1976*a*). The analogous bromide, iodide, or compounds with other S/Hal ratios seem not to exist at the S-rich parts of the corresponding Bi_2S_3–$BiHal_3$ systems. To elucidate the structural relationships between $Bi_4Cl_2S_5$ and the above compounds its crystal structure was determined.

The vapour-grown crystals were black, elongated-hexagonal prisms. Intensities from a single crystal (56 × 65 × 300 μm) were collected on an automatic four-circle diffractometer (Enraf–Nonius CAD-4) with graphite-monochromatized Mo $K\alpha$ radiation and an ω–2θ scan mode.

The correct space group $R\bar{3}$, replacing the previously reported $R\bar{3}m$, $R3m$, or $R32$ (Krämer, 1976*a*), was determined by comparison of the intensity distributions in point groups $\bar{3}$ and $\bar{3}m$. The former yields an internal R of 8·7%, the latter 52%.

Calculations were performed with the XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *MULTAN* systems (Main, Lessinger, Woolfson, Germain & Declercq, 1977). 3052 independent reflexions were measured, 1153 of which had $I > 3\sigma(I)$. Intensities were corrected for absorption by the program *ORABS*, which computes transmission factors and mean path lengths by Gaussian integration.

The four Bi positions were located with *MULTAN*. Subsequent Fourier maps yielded six anion positions. Refinement on all positional, isotropic extinction, and anisotropic thermal parameters resulted in a final R = 0·056* and an average shift/error of $1{\cdot}4 \times 10^{-2}$.

Table 1. *Fractional atomic coordinates* (×10^4)

	x	y	z
Bi(1)	2186 (1)	307 (1)	770 (2)
Bi(2)	2124 (1)	259 (1)	3932 (2)
Bi(3)	1730 (1)	2387 (1)	2512 (2)
Bi(4)	0	0	2666 (5)
X(1)	817 (6)	1520 (6)	859 (10)
X(2)	3041 (7)	2213 (7)	752 (11)
X(3)	4502 (6)	4109 (6)	783 (9)
X(4)	4994 (8)	2519 (8)	990 (10)
X(5)	2529 (7)	3714 (8)	986 (10)
X(6)	758 (6)	1366 (7)	4009 (10)

Table 2. *Interatomic distances* (Å)

Bi(1)–X(1)	2·73 (2)	Bi(2)–X(2)	3·08 (1)
	2·66 (2)	X(3)	2·70 (1)
X(2)	2·95 (3)		3·66 (2)
	3·28 (1)	X(4)	2·62 (2)
	3·34 (1)	X(5)	3·28 (3)
X(4)	2·62 (2)	X(6)	2·65 (2)
X(5)	3·41 (1)		3·20 (2)
Bi(3)–X(1)	2·70 (1)	Bi(4)–X(1)	3·44 (1) ×3
X(2)	3·53 (2)	X(4)	2·90 (1) ×3
X(3)	2·62 (2)	X(6)	2·88 (1) ×3
	3·05 (2)		
X(4)	3·07 (2)		
X(5)	2·97 (1)		
	3·50 (2)		
X(6)	2·71 (1)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33943 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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