

The Crystal Structure of Cesium Dimethyldithiocarbamate, $\text{CsS}_2\text{CN}(\text{CH}_3)_2$

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The crystal structure of the titel compound was determined from three-dimensional diffractometer X-ray data. The crystals are orthorhombic with $a = 9.836(2)$ Å, $b = 11.138(2)$ Å, $c = 6.797(1)$ Å and $Z = 4$. The most probable space group is $Cmcm$, $R = 0.053$. The metal atoms and the ligand groups are packed in chains parallel to c . Within a chain each cesium atom has two sulfur atoms at a distance of $3.636(1)$ Å and four at $3.713(1)$ Å. The chains are connected by two long Cs—S bonds of $4.099(1)$ Å from each cesium so that a three-dimensional coordination net is formed with cesium in eight-coordination. The dimethyldithiocarbamate ligand has mm symmetry.

Compounds of the composition AX are being studied at this Institute. A is a monovalent cation and X is an organic ligand containing sulfur, e.g. dialkyldithiocarbamate [S_2CNR_2], etc. Hitherto A has usually been Cu(I), Ag(I), Au(I), or Tl(I). A dte with the alkyl group R is abbreviated: M (methyl), E (ethyl), nP (propyl), iP (1-methylethyl), nB (butyl), iB (2-methylpropyl). In many cases compounds of Tl(I) and the alkali metals are similar. In the crystal structures of TIM¹ and TlnB² layers, and of TIE,³ TlnP,⁴ TliP,⁵ and TliB⁶ chains are formed. CsnB⁷ is a layer structure related to TlnB. Uhlin⁸ has studied dte of the alkali metals in solution.

EXPERIMENTAL

Crystal preparation. The titel compound, CsM, was prepared by the general procedure described by Uhlin.⁸ The solid residue was recrystallized from 2-propanol. This solvent had been prepared by drying 99.5 % 2-propanol with Union Carbide Molecular Sieves 3 Å.

Crystal data. The crystals appear as long yellow prisms elongated along [001] with the faces (110) and $\bar{1}\bar{1}0$ developed. The density was measured by flotation in a mixture of CHCl_3 and CHBr_3 . The unit cell dimensions were found from a powder photograph taken on an IRDAB XCD 700 camera using $\text{CrK}\alpha_1$ radiation ($\lambda = 2.28962$ Å) with silicon ($a = 5.43054$ Å) as an internal standard. The cell parameters were refined by the least-squares method using 22 observed θ -values. **Crystal data:** Orthorhombic, space groups: $Cmcm$ (No. 63), $C2cm$ (No. 40) or $Cmc2_1$ (No. 36), $a = 9.836(2)$ Å, $b = 11.138(2)$ Å, $c = 6.797(1)$ Å, $V = 744.7$ Å³, $Z = 4$, $D_m = 2.26$ gm⁻³, $D_x = 2.257$ gm⁻³, m.p. = 169–173 °C, $\mu(\text{MoK}\alpha) = 54.8$ cm⁻¹.

Intensity data. A crystal of dimensions $0.060 \times 0.058 \times 0.150$ mm³ was mounted in a thin-walled glass capillary. The measurements were made on a Stoe-Philips four-circle PDP8/I computer-controlled diffractometer with a graphite monochromator using $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å) and an ω - 2θ scan technique. Automatic filter selection (one filter having a cutdown of 2:1 was inserted for the five strongest reflexions) and automatic scan-speed selection ($\times 1$, $\times 2$ or $\times 4$) was used. 1283 intensities giving 1137 independent reflexions were collected in one octant in the reciprocal space up to $\sin \theta/\lambda = 0.862$. Three standard reflexions 004, 042 and 510 were monitored every 40 reflexions. ω - 2θ - and χ -scan over some reflexions before and after the experiment showed mechanical stability of the crystal mounting and the diffractometer system, and verified the quality of the detector crystal.

Corrections were made for background, Lorentz and polarization effects (including monochromator polarization) and for absorption. The transmission factor varied between 0.70 and 0.75. Isotropic extinction corrections were applied during the least-squares refinement.

Structure determination and refinements. The positions of cesium and sulfur were obtained from the three-dimensional Patterson function.

Table 1. Atomic coordinates and thermal parameters. The anisotropic factor is defined as $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. $\beta_{13} = \beta_{23} = 0.0$. Estimated standard deviations (in parentheses) are given for the last digits.

Atom	x	y	z	B
Cs	0.0	0.15042(3)	0.25	
S	0.34797(8)	0.35292(7)	0.25	
C	0.5	0.2773(3)	0.25	
N	0.5	0.1569(3)	0.25	
Cl	0.3734(4)	0.0891(3)	0.25	
H1	0.388(8)	0.011(6)	0.25	9.9(2.1)
H2	0.317(4)	0.113(3)	0.367(6)	5.4(8)

Atom	β_{11}	β_{22}	β_{33}	β_{12}
Cs	0.00981(4)	0.00750(3)	0.01396(6)	0.0
S	0.00697(6)	0.00659(6)	0.01997(16)	0.00157(5)
C	0.0063(3)	0.0051(3)	0.0118(6)	0.0
N	0.0061(3)	0.0052(2)	0.0244(9)	0.0
Cl	0.0075(3)	0.0068(3)	0.0375(13)	-0.0009(2)

The nitrogen and carbon atoms were then located in an F_0 -synthesis, assuming the centrosymmetric space group $Cmcm$. Atomic positions and isotropic temperature factors were refined by full matrix least-squares calculations. After introduction of anisotropic temperature factors and of an isotropic extinction parameter, the hydrogen atoms were found in a Fourier difference synthesis. In the final cycles of the refinement, the coordinates for all atoms, the thermal parameters, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms were allowed to vary (33 parameters in all). The final shifts were all smaller than 1% of σ . The resulting positional and thermal parameters are given in Table 1. A list of observed and calculated structure amplitudes is available on request. The quantity minimized in the least-squares refinements was $\sum w(|F_o^h| - |F_c^h|)^2$. The reflexions were weighted according to the formula $w^{-1} = \sigma_c^2(F^h) + 0.03|F_o^h| = \sigma^2(F^h)$. Using all the 1137 reflexions, the refinement converged at $R(F^h) = \sum ||F_o^h| - |F_c^h|| / |F_o^h| = 0.064$ and $R_w(F^h) = (\sum w(|F_o^h| - |F_c^h|)^2 / \sum w|F_o^h|)^{1/2} = 0.073$ corresponding to a conventional $R(F)$ based on F of 0.053. This resulted in 49 reflexions having $||F_o^h| - |F_c^h|| / \sigma(F^h) > 2.0$ with the extreme value of 20 for the strongest reflexion 002. The value $q = (\text{number of observations}) / (\text{number of parameters}) = 34$. The scattering factors for Cs were taken from the tables provided by Cromer and Waber,⁹ and for S, N and C those suggested by Hanson *et al.*¹⁰ The spherical scattering factors proposed by Stewart *et al.*¹¹ were used for H. Anomalous dispersion corrections¹² ($\Delta f'$ and $\Delta f''$) were applied for Cs and S.

Attempts were made to break the symmetry and to perform the refinement in the space groups $C2cm$ and $Cmc2_1$. No reasonable structure alternative was, however, obtained by these efforts. The space group used, $Cmcm$, gives good agreement between observed and calculated intensities and very satisfactory atomic positions even for the hydrogen atoms.

All large calculations were performed using the IBM 370/155 computer in Uppsala. The following major programs were used: CELNE, DATAPH, SORTA, DRF, UPALS, DISTAN and ORTEP. These programs have been described by Lundgren.¹³ Small calculations were performed using the departmental IBM 1800 computer.

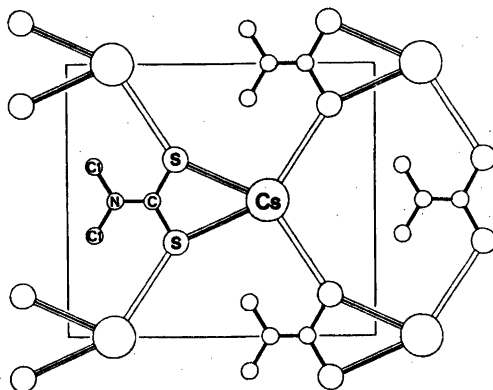


Fig. 1. Arrangement of the non-hydrogen atoms in the mirror plane $z = 1/4$.

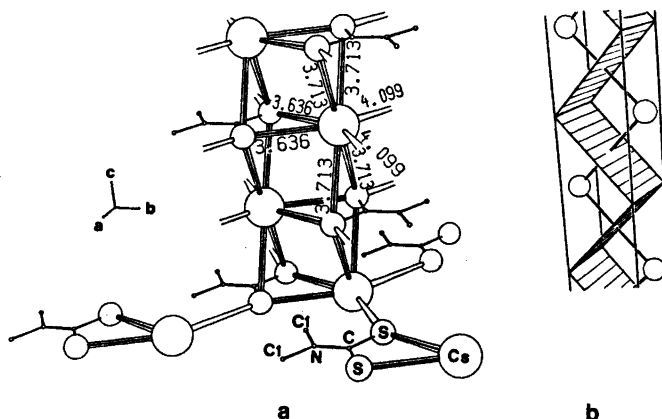


Fig. 2. a. A chain perpendicular to the layer in Fig. 1. b. A schematical representation of the cesium and sulfur atom arrangement in a chain.

RESULTS AND DISCUSSION

General. The non-hydrogen atoms are situated in mirror planes (Fig. 1). Two such layers ($z=1/4$, $z=3/4$) related by a centre of symmetry ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) give the contents of the unit cell. The crystal structure can be described as built up of chains, perpendicular to these layers. The chains are thus parallel to c (Fig. 2). Cesium is coordinated to sulfur atoms in three dithiocarbamate ligands giving six Cs-S bonds within the chain. Two further sulfur atoms situated in adjacent chains are coordinated at an appreciably longer distance. Thus, cesium coordinates eight sulfur atoms. The coordination polyhedron for cesium is a distorted cube. Interatomic distances and angles are collected in Table 2.

Intermolecular contacts. There are no intermolecular distances shorter than the sum of

the radii defined by Bondi¹⁴ or those recommended by van der Helm *et al.*¹⁵ The distances to nonbonding atoms in the vicinity of cesium are reported, as no values are given for Cs⁺ by the cited authors. Short distances can be expected between atoms in adjacent mirror planes, as the distance between the mirror planes $z=1/4$ and $z=3/4$ is 3.40 Å. Distances Cs-N (4.02 Å) and Cs-C (3.49 Å) are of this type. Methyl hydrogen H2 are situated 3.25 Å from cesium (in adjacent chains). The corresponding Cs-Cl distance is 3.74 Å.

Coordination. The coordinating distances exceed the sum of the Pauling ionic radii, 3.53 Å. The two shortest Cs-S distances [3.656(1) Å] are found in the dithiocarbamate plane and four slightly longer [3.713(1) Å] in the chain direction. These six distances, which are longer than those found for six-coordinated cesium in Cs₂NB,¹³ average value 3.62 Å, agree well with the mean Cs-S distance, 3.66 Å, in Cs₂CS₂·H₂O,¹⁶ where cesium coordinates nine atoms (sulfur and oxygen). A mean value of 3.67 Å for eight-coordination is found in Cs₂Pd₂S₄¹⁷ and Cs₂Mn₂S₄.¹⁸ The same value appears in Cs₂S₄¹⁹ for distances less than 4 Å. The non-substituted dithiocarbamates of cesium, rubidium, potassium, and ammonium are isostructural.^{20,21} The cation is eight-coordinated as in CsM, but the coordination problems are quite different since the shielding bulks are replaced by hydrogens suitable for hydrogen bonds.

Table 2. Interatomic distances (Å) and angles (°).

Cs-Cs	4.773(1)	S-C-S	121.2(2)
Cs-S	3.636(1)	S-C-N	119.4(2)
Cs-S	3.713(1)	C-N-Cl	121.2(2)
Cs-S	4.099(1)	Cl-N-Cl	117.5(4)
S-S	2.991(2)	N-Cl-H1	112(5)
C-S	1.716(2)	N-Cl-H2	110(2)
C-N	1.342(5)	H1-Cl-H2	110(3)
N-Cl	1.456(4)	H2-Cl-H2	105(4)
Cl-Cl	2.490(8)		
H1-Cl	0.88(6)		
H2-Cl	1.00(4)		

The chain. Fig. 2b shows the sulfur atoms in a chain represented by a series of rectangles. The cesium atoms are situated 0.04 Å outside the columns of sulfur atoms, and form a planar equidistant zigzag chain with Cs—Cs—Cs angles of 90.8°. The Cs—Cs distance, 4.773 Å, is longer than the one found in Cs₂N₂, 4.29 Å. In the cesium halides, the metal-metal distances have values of 4.1 Å to 4.3 Å, whereas the distance is 5.265 Å in solid cesium.²² The present type of chain is also found in TIE.³

The linkage of the chains. The bonds from the chain in Fig. 2a demonstrate how adjacent chains are connected. Cesium coordinates one sulfur atom in each of two neighbouring chains at a distance of 4.099(1) Å. Although these two distances are significantly longer than those previously discussed, all the eight bonds contribute to the lattice energy because of the ionic character of the Cs—S interaction.

The ligand. The dimethyldithiocarbamate ligand has *mm* symmetry. In CsM the C—N distance is about 0.02 Å longer, and the S—C—S angle is about 10° larger than in the ligand in CuM,²³ TiM₂Cl,²⁴ CoM₂NO,²⁵ and FeM₂NO (−80 °C).²⁶

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