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Short Communications

Least Squares Refinement of the Molecular Structure of Cesium Hexasulphide

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Abrahams and Grison[1] in 1953 published the crystal structure of cesium hexasulphide. From their results, based on positional parameter refinement by double Fourier series, the bond lengths in the hexasulphide ion are: $S_1-S_2=1.99$ Å, $S_2-S_3=2.10$ Å, $S_3-S_4=2.03$ Å, $S_4-S_5=2.12$ Å, and $S_5-S_6=2.03$ Å, each ± 0.03 Å. The dihedral angles of the valencies in the sulphur chain were found to be: $S_1S_2S_3/S_2S_3S_4=78.6°$, $S_2S_3S_4/S_3S_4S_5=81.9°$ and $S_3S_4S_5/S_4S_5S_6=61.4°$. The authors concluded that in a polysulphide chain there are alternating long and short bonds, the two sulphide electrons being localized in the short bonds. Thus in the hexasulphide ion the three short bonds were assumed to possess one third double bond character, and the two long bonds should then be pure single bonds.

One of us (A. H.)[2] has recently pointed out that the sulphur-sulphur bond length varies with the dihedral angle. 2.10 Å seems to be the relevant length for the S–S single bond in a *cis* planar disulphide group, and bond lengths of about 2.03 Å are usually found when the dihedral angle is about 90°. The variation in sulphur-sulphur bond length with dihedral angle may be partly due to lone pair repulsion, which is most pronounced when the disulphide group is *cis*-planar, *i.e.*, when the dihedral angle is zero, and partly due to π-bonding through *p-d* overlap, presumably most pronounced at dihedral angles near 90°.

The bond lengths and dihedral angles reported by Abrahams and Grison[1] for the hexasulphide ion do not fit into the above picture, and we therefore thought it worth while to refine the structure of cesium hexasulphide by a different

Table 1. Final atomic coordinates from the least squares refinement.

Atom	*x*	*y*	*z*
$Cs^+(1)$	0.09600	0.32577	0.05004
$Cs^+(2)$	0.38603	−0.30912	0.10022
$S^-(1)$	0.14867	−0.34207	0.52607
S(2)	0.10231	−0.13434	0.50792
S(3)	0.21304	−0.01251	0.79513
S(4)	0.37004	0.02700	0.63828
S(5)	0.36479	0.20809	0.35704
$S^-(6)$	0.32969	0.38642	0.58597

Table 2. Final temperature parameters β_{ij}. The expression used is $\exp-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+kl\beta_{23}+hl\beta_{13})$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
$Cs^+(1)$	0.0041	0.0070	0.0262	−0.0002	−0.0029	0.0039
$Cs^+(2)$	0.0040	0.0049	0.0269	−0.0031	−0.0021	0.0010
$S^-(1)$	0.0059	0.0040	0.0275	0.0008	−0.0029	0.0161
S(2)	0.0036	0.0036	0.0270	−0.0060	0.0011	−0.0012
S(3)	0.0071	0.0040	0.0221	−0.0040	−0.0032	0.0056
S(4)	0.0042	0.0035	0.0382	0.0026	0.0033	0.0123
S(5)	0.0055	0.0035	0.0186	−0.0079	−0.0108	0.0043
$S^-(6)$	0.0057	0.0011	0.0397	−0.0048	−0.0034	0.0014

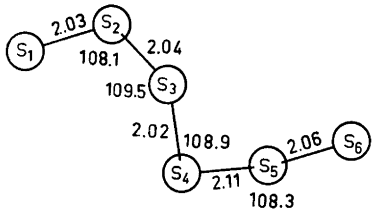

Fig. 1. Bond lengths (Å) and bond angles (°) in the hexasulphide ion.

procedure. A least squares refinement of the structure, based on the structure factor data published by Abrahams and Grison,[1] has been carried out on the IBM 1620 II computer using Mair's[3] program.

Atomic coordinates and temperature parameters from the least squares refinement are listed in Tables 1 and 2, and corresponding bond lengths and bond angles in the hexasulphide ion are given in Fig. 1. The standard deviation in bond lengths is 0.03 Å and in angles 1.3°. The dihedral angles are found to be: $S_1S_2S_3/S_2S_3S_4=74.6°$, $S_2S_3S_4/S_3S_4S_5=83.1°$ and $S_3S_4S_5/S_4S_5S_6=60.9°$.

Our value for the length of the S_2-S_3 bond is 0.06 Å smaller than the value reported by Abrahams and Grison. The S_4-S_5 bond is also by the present refinement found to be the longest in the sulphur chain. This may be explained by taking into account the dependence of sulphur-sulphur bond length on dihedral angle; the dihedral angle associated with S_4-S_5 is as low as 60.9°.

On the basis of the dihedral angles and the bond-length/dihedral-angle relationship,[2] the values predicted for the lengths of the three central bonds in the hexasulphide ion are: $S_2-S_3=2.04$ Å, $S_3-S_4=2.03$ Å, and $S_4-S_5=2.07$ Å. These agree within the error with the bond lengths in Fig. 1.

1. Abrahams, S. C. and Grison, E. *Acta Cryst.* **6** (1953) 206.
2. Hordvik, A. *Acta Chem. Scand.* **20** (1966) 1885.
3. Mair, G. A. *Structure Factor and Least Squares Programs for the IBM 1620* II, Pure Chemistry Division, National Research Council, Ottawa, Canada 1963.

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On the Molecular Structure of Di-cyclopentadienylberyllium $(C_5H_5)_2Be$

II. Least Squares Refinement

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The molecular structure of gaseous dicyclopentadienylberyllium as determined by Almenningen, Bastiansen and Haaland [1] by means of electron diffraction is shown in Fig. 1. The molecule consists of two regular C_5H_5 rings that lie parallel and staggered with a vertical ring-to-ring distance of $h=3.37\pm0.03$ Å. The beryllium atom was found to occupy a position on the fivefold symmetry axis $h_1=1.485\pm0.005$ Å from one ring and $h_2=1.980\pm0.010$ Å from the other. The molecular symmetry is thus C_{5v}.

Since Almenningen *et al.*[1] found it necessary to invoke shrinkage effects of the order of 0.1 Å in order to obtain satisfactory agreement with the experimental data, and since the molecular structure is highly unusual, we have considered it worth while to repeat the structure determination using the experimental material of Almenningen *et al.*[1] and the more advanced calculation methods that now are available.

The complex atomic scattering factors $f(s)=|f(s)|\exp(i\eta(s))$ of H, Be, and C were computed under the partial wave approximation with a program written by Peacher.[2] The experimental intensities recorded by Almenningen *et al.*[1] had been

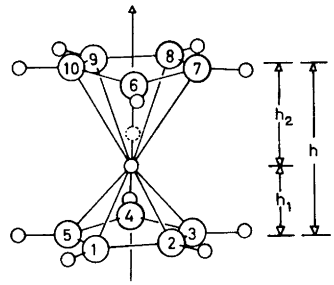

Fig. 1. The molecular structure of $(C_5H_5)_2$ Be with the two positions of the beryllium atom drawn in.