[CONTRIBUTION FROM THE LABORATORY FOR INSULATION RESEARCH, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Crystal Chemistry of Cesium Penta- and Hexasulfide[1]

BY S. C. ABRAHAMS, E. GRISON AND J. KALNAJS

RECEIVED DECEMBER 26, 1951

Cesium hexasulfide has been prepared by disproportionation of Cs_2S_5 in aqueous ethyl alcohol[2] and its crystal structure determined. Cs_2S_5, obtained by dehydration of $Cs_2S_5 \cdot H_2O$, has been shown to possess a crystal structure similar to that of Cs_2S_6.

Experimental

Cs_2S_5 was prepared by a method similar to that of Biltz, *et al.*,[3] in which stoichiometric amounts of elementary sulfur are added to Cs_2S in solution. A dilute solution of CsOH was obtained from pure Cs_2SO_4 by exchange with $Ba(OH)_2$. This and all succeeding operations were carried out under a H_2, N_2 or He atmosphere. The solution was concentrated to approximately 3 *N* in a Pt dish. One-half was then saturated with pure H_2S, and the resulting CsHS solution mixed with the remaining half of the CsOH, taking care to maintain stoichiometric proportions by direct analysis. The solution of Cs_2S thus obtained was colorless; oxidation results in a yellow coloration. Sulfur had an appreciable solubility in this solution at room temperature, but the reaction with Cs_2S proceeded best when the solution was slowly raised to the b.p. After some concentration by distillation in H_2, the deep red solution was allowed to evaporate further in a desiccator in an atmosphere of H_2. A period of 10–20 hr. sufficed to obtain large, coral-red crystals. These crystals were then washed with 75% alcohol and dried *in vacuo*, with a yield of 60–75%. Their analysis unambiguously corresponds to the molecular formula $Cs_2S_5 \cdot H_2O$. The small variation in the water content appeared to depend upon the temperature and concentration of the mother liquor. The shining facets of the hydrate crystals rapidly dulled on exposure to air, and in a few days became coated with small white crystals. The composition of this oxidation product was identified by chemical analysis and from the X-ray powder pattern as $Cs_2S_2O_3$ and rhombic S. The water content of crystalline $Cs_2S_5 \cdot H_2O$ diminished on drying. It became zero on slowly raising the temperature *in vacuo*, the resulting Cs_2S_5 having a m.p. of 210°[4] and a density of 2.93. The density increased to 3.13 on fusing the Cs_2S_5.

	Analyses, %			
Sample	1	2	3	Calcd. for $Cs_2S_5 \cdot H_2O$
Cs	59.44	59.21	59.44	59.84
S	36.32	35.73	35.75	36.09
H_2O	3.96	4.86	3.83	4.05
Cs:S	2:4.998	2:5.02	2:4.986	2:5.000

Solution of $Cs_2S_5 \cdot H_2O$ in 70% alcohol and subsequent evaporation to the point of crystallization usually[5] produced prismatic, brown-red needles of Cs_2S_6. Their analysis corresponds to a molecular formula of *ca.* $Cs_2S_{5.42}$. These crystals had a strong odor of H_2S, and were also readily oxidized to $Cs_2S_2O_3$. Variations in the density of a number of crystals, from 3.076 to 3.03, suggest that the chemical composition is not uniform along the needle length. The fairly large crystals (*ca.* 0.5 mg.) used in the semi-microanalysis might therefore contain appreciable amounts of lower polysulfide, which could account for the low S:Cs ratio. However, a complete crystal structure determination of this salt[6] has unambiguously shown it to consist primarily of Cs_2S_6.

	Analyses, %			
Sample	1	2	3	Calcd. for Cs_2S_6
Cs	58.97	58.85	60.62	57.92
S	38.64	39.05	39.30	42.08
H_2O	0.75	0.22	0.00	0.00
Cs:S	2:5.43	2:5.50	2:5.36	2:6.00

$Cs_2S_5 \cdot H_2O$ crystallizes as large, coral-red, triclinic prisms, terminated with many well-developed facets: $a = 6.91$, $b = 7.81$, $c = 10.14$ Å., $\alpha = 103°32'$, $\beta = 108°10'$, and $\gamma = 97°50'$. The measured density is 2.94, corresponding to 2 molecules per unit cell. The space group was assumed to be $P\bar{1}$. The crystals had an m.p. of 85°.

Cs_2S_5 was obtained on dehydration of $Cs_2S_5 \cdot H_2O$ by heating *in vacuo* to *ca.* 80° for 10 hours (no S was lost in this process). The coral red powder thus produced gave an X-ray pattern of marked similarity to that of Cs_2S_6. A single crystal of $Cs_2S_5 \cdot H_2O$ was then examined with a precession camera, after careful dehydration. Records were made of two zones which very closely corresponded in spacings and intensities to the $\{h0l\}$ and $\{0kl\}$ zones in Cs_2S_6. The angle between these zones was within 5° of the corresponding angle in Cs_2S_6. Hence these data tend to confirm the similarity in the crystal structure of Cs_2S_5 and Cs_2S_6.

Cs_2S_6 forms fine, small, brown-red, triclinic needles: $a = 11.53$, $b = 9.17$, $c = 4.67$ Å., $\alpha = 89°9'$, $\beta = 95°15'$ and $\gamma = 95°7'$. The measured density is 3.076, again corresponding to 2 molecules per unit cell. The space group was taken as $P\bar{1}$. These crystals melted at 185°. It may be noted that the volumes of the unit cells of $Cs_2S_5 \cdot H_2O$ and Cs_2S_6 (492.5 and 489.4 Å^3., resp.) are within 1% of each other. The limit of error in the cell sides and angles of both crystals is estimated as ±0.02 Å. and ±0.5°, respectively.

Discussion

Two observations require comment: the formation of Cs_2S_6 from $Cs_2S_5 \cdot H_2O$ by disproportionation in aqueous alcohol, and the similarity in the crystal structure of Cs_2S_6 and Cs_2S_5.

The production of Cs_2S_6 indicates that $S_6^=$ ions must be present in the solution of $Cs_2S_5 \cdot H_2O$, and hence lower polysulfide ions as well, since no elementary sulfur is observed on dissolving the $Cs_2S_5 \cdot H_2O$ crystals. Thus a complex equilibrium between $S_6^=$, $S_5^=$, and one or more lower polysulfides must exist, which is displaced in the direction of hexasulfide formation by the conditions in the aqueous alcoholic solution. In attempts to influence this equilibrium by the addition of elementary sulfur to the solution, it was observed that the sulfur dissolved on warming, but reappeared on cooling.

In the crystal structure of Cs_2S_6[6] the anion consists of a non-branched, non-planar, six-membered chain of sulfur atoms. These chains are connected by van der Waals contacts of 3.40 Å. to form helices of sulfur atoms which extend throughout the crystal, with the cesium atoms spaced around them. Thus, when the water of crystallization is removed from the $Cs_2S_5 \cdot H_2O$ lattice, it seems likely that the $S_5^=$ ion will assume a spatial configuration very similar to the $S_6^=$ ion in Cs_2S_6 with respect to the cesium atoms. In this case, the pentasulfide helix may have to be somewhat more extended in order to maintain a similar charge distribution in the crystal.

CAMBRIDGE, MASSACHUSETTS

---

(1) Sponsored by the ONR. the Army Signal Corps, and the Air Force under ONR Contracts N5ori-07801 and N5ori-07858.

(2) J. G. Pearson and P. L. Robinson (*J. Chem. Soc.*, 1983 (1931)) obtained polysulfides with a maximum S content corresponding to $Cs_2S_{4.119}$ by dissolving S in fused Cs_2S.

(3) W. Biltz and E. Wilke-Dörfurt, *Ber.*, **38**, 123 (1905).

(4) All temperature measurements are uncorrected and are ±1°.

(5) Occasionally sulfur was precipitated, in which case the product was discarded.

(6) S. C. Abrahams and E. Grison, to be published.