Die aus den röntgenographischen Angaben berechnete Dichte ϱ ist bei α-$Cu(NH_3)_2Br_2$, sowie β-$Cu(NH_3)_2Br_2$: 3,200 g.cm.$^{-3}$.

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The Crystal Structure of Cesium Tetrabromozincate, Cs_2ZnBr_4

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The crystal structure of Cs_2ZnBr_4 has been determined by three-dimensional Fourier (difference) methods. The structure is essentially the same as that of Cs_2ZnCl_4, with 4 molecules in a cell of dimensions $a_0 = 10{\cdot}196$, $b_0 = 7{\cdot}770$, $c_0 = 13{\cdot}517$ Å, space group *Pnma*. The $ZnBr_4^{-2}$ tetrahedron is appreciably distorted by the steric 'pressure' of one neighboring Cs^+ ion.

Introduction

The crystal structure of Cs_2CoCl_4 has been reported by Poraj-Koshitz (1956) and Cs_2ZnCl_4 has been shown to be isomorphous by Brehler (1957). The reported structure is of the K_2SO_4 type, containing tetrahedral MX_4^{-2} ions. Cs_2CuCl_4 has a structure (Helmholtz & Kruh, 1952) which is quite similar except for a marked distortion of the $CuCl_4^{-2}$ group. We are at present investigating other structures of the type Cs_2MBr_4 and report at this time the crystal structure of Cs_2ZnBr_4.

Experimental

Crystals of Cs_2ZnBr_4 were grown by evaporation at room temperature of an aqueous solution containing stoichiometric proportions of CsBr and $ZnBr_2$. The colorless, orthorhombic crystals were lath-like, bounded by (011) and (001) and terminated by (100).

Precession and equi-inclination Weissenberg photographs were taken with copper $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å).

The following cell dimensions were obtained by superimposing NaCl ($a_0 = 5{\cdot}63874$ Å) rotation photographs on the same films with Cs_2ZnBr_4 rotation and Weissenberg photographs.

$$a_0 = 10{\cdot}196 \pm 0{\cdot}018,\; b_0 = 7{\cdot}770 \pm 0{\cdot}006,\; c_0 = 13{\cdot}517 \pm 0{\cdot}023 \text{ Å}.$$

Systematic absences of $(0kl)$ for $k+l$ odd and of $(hk0)$ for h odd indicated the space group to be *Pnma* or $Pn2_1a$.

Comparison of the axial ratios of Cs_2ZnCl_4 (1·317:1·000:1·755; Brehler, 1957) and Cs_2ZnBr_4 (1·312:1·000:1·730) and also of the general appearance of their Weissenberg photographs suggests that the structures are similar. Therefore the space group *Pnma* with 4 molecules per cell was initially assumed and later verified by the final structure.

Partial three-dimensional data (i.e. $h0l$ through $h5l$) were collected by means of a non-integrating Weissenberg camera. The number of observed reflections was 553. The diffraction spots were scanned by means of a photometer and relative peak heights were obtained and used as intensities, being placed on an absolute scale by comparison with calculated values at a later stage of the structure determination.

Correction for absorption was made by interpolation from the table given by Bradley (1935); Lorentz and polarization factors were applied and structure factors calculated using Thomas & Umeda (1957) scattering factors. Calculations were carried out on an IBM type 650 computer.

Determination of the structure

Initial coordinates used were those for Cs_2ZnCl_4 (Brehler, 1957), and refinement of positions and temperature factors proceeded by a few Fourier sections and several difference syntheses. A final reliability index of 0·114* was obtained. The reliability index for special classes of reflections are as follows:

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* The table of calculated and observed structure factors may be obtained from E. C. Lingafelter.

$h0l$: 0·125
$h1l$: 0·119
$h2l$: 0·092
$h3l$: 0·112
$h4l$: 0·109
$h5l$: 0·150

$h+l=2n$, $k=2n$: 0·117
$h+l=2n$, $k=2n+1$: 0·113
$h+l=2n+1$, $k=2n$: 0·100
$h+l=2n+1$, $k=2n+1$: 0·127

Atomic positions and individual isotropic temperature factors are listed in Table 1. All atoms are in positions (4*c*) except Br_3 which is in (8*d*). The standard deviations in the parameters, calculated according to Cruickshank (1949), are 0·004 Å for Cs, 0·008 for Zn, and 0·007 for Br.

Table 1. *Atomic positional parameters and temperature factors for* Cs_2ZnBr_4

	x	y	z	B
Cs_1	0·6378	0·2500	0·3966	5·100
Cs_2	0·4766	0·2500	0·8284	2·500
Zn	0·2356	0·2500	0·4214	2·500
Br_1	0·0030	0·2500	0·4021	3·300
Br_2	0·3109	0·2500	0·5904	3·650
Br_3	0·3255	0·0000	0·3461	4·550

Discussion

The crystal structure of Cs_2ZnBr_4 is essentially the same as that of Cs_2ZnCl_4, consisting of Cs^+ and tetrahedral $ZnBr_4^{-2}$ ions. Bond lengths and angles in the $ZnBr_4^{-2}$ are listed in Table 2, along with their standard deviations. The average Zn–Br distance, 2·391 Å ($\sigma=0{\cdot}01$ Å) may be compared with 2·38 Å found in $Zn(NH_3)_2Br_2$ (MacGillavry & Bijvoet, 1936).

Table 2. *Bond lengths and angles in* Cs_2ZnBr_4

$ZnBr_1$	2·386 Å ± 0·010	Br_1ZnBr_2	114·9 ± 0·37°
$ZnBr_2$	2·410	Br_1ZnBr_3	109·7
$ZnBr_3$	2·377	Br_2ZnBr_3	106·4
		Br_3ZnBr_3	109·6

The $ZnBr_4^{-2}$ tetrahedron appears to be significantly distorted, the difference (5·4°) between the Br_1ZnBr_2 angle and the normal tetrahedral angle being more than ten times the standard deviation. The appearance of this large angle coupled with the small angle between Br_2 and the two Br_3 atoms indicates that Br_2 has been displaced from its normal tetrahedral position. The significance of this displacement becomes apparent upon consideration of the temperature factors and environment of the Cs^+ ions. The distances to the nearest neighboring Br^- for each Cs^+ ion are listed in Table 3. It is to be noted that seven (7) neighboring Br^- ions of Cs_2 are closer to it than the nearest neighbor of Cs_1. This is evidently the reason for the temperature factor of Cs_2 being so much smaller than that of Cs_1. Further, the nearest neighbor of Cs_2 is Br_2 at a distance of 3·581 Å, slightly closer than the Cs–Br distance (3·615 Å; Shulz, 1951) found in CsBr. Thus it seems apparent that the distortion of the $ZnBr_4^{-2}$ tetrahedron is caused by the pressure of the Cs_2^+ ion.

Table 3. *Neighboring bromide ions*

x	y	z	Dist. (Å)
$Cs_{(1)}$ at 0·6378, ¼, 0·3966			
1·0030	¼	0·4021	3·724
0·3255	0	0·3461	3·792
0·3255	½	0·3461	
0·6891	¾	0·4096	3·924
0·6891	−¼	0·4096	
0·6745	½	0·6539	4·001
0·6745	0	0·6539	
0·3109	¼	0·5904	4·239
0·8255	½	0·1539	4·265
0·8255	0	0·1539	
0·5030	¼	0·0979	4·266
$Cs_{(2)}$ at 0·4766, ¼, 0·8284			
x	y	z	Dist. (Å)
0·8109	¼	0·9096	3·581
0·3109	¼	0·5904	3·634
0·1745	½	0·8461	3·649
0·1745	0	0·8461	
0·5030	¼	1·0979	3·653
0·6745	½	0·6539	3·662
0·6745	0	0·6539	
0·4970	¾	0·9021	4·016
0·4970	−¼	0·9021	

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