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The Crystal Structure of Cesium Tetrabromocuprate(II)

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The crystal structure of Cs_2CuBr_4 has been determined by three-dimensional Fourier (difference) methods. The structure is essentially the same as that of Cs_2CuCl_4, with 4 molecules in a cell of dimensions

$$a_0=10\cdot195,\ b_0=7\cdot965,\ c_0=12\cdot936\ \text{Å}\ ,$$

space group *Pnma*. The Jahn–Teller distortion of the $CuBr_4^{-2}$ tetrahedron is considerable, yielding bond angles of 128° and 101°.

Introduction

The crystal structure of Cs_2ZnBr_4 has been reported by Morosin & Lingafelter (1959) and was shown to be similar to that of Cs_2CoCl_4 (Poraj-Koshitz, 1956) and of Cs_2ZnCl_4 (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 reporting at this time the crystal structure of Cs_2CuBr_4 which is very similar to Cs_2CuCl_4 and which has a somewhat greater distortion of the $CuBr_4^{-2}$ ion.

Experimental

Crystals of Cs_2CuBr_4 were grown by evaporation at room temperature of an aqueous solution containing stoichiometric proportions of CsBr and $CuBr_2$. The dark brown orthorhombic crystals are prisms bounded by (100), (001), (101), (103) and terminated by (010), (011), and (111).

Precession and equi-inclination Weissenberg photographs were taken with copper $K\alpha$ radiation ($\lambda=1\cdot5418$ Å).

The following cell dimensions were obtained by superimposing NaCl ($a_0=5\cdot63874$ Å) rotation photographs on the same films with Cs_2CuBr_4 rotation and Weissenberg photographs.

$$a_0=10\cdot195\pm0\cdot012,\ b_0=7\cdot965\pm0\cdot005\ ,$$
$$c_0=12\cdot936\pm0\cdot015\ \text{Å}\ .$$

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

$$Cs_2CuCl_4\ (1\cdot269:1\cdot000:1\cdot614)$$

and of

$$Cs_2CuBr_4\ (1\cdot280:1\cdot000:1\cdot624)$$

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 Nonius integrating Weissenberg camera, integrating in one direction only. The number of reflections measured in this way was 394. The diffraction spots were scanned in a direction normal to that of the camera integration by means of a photometer and relative areas were planimetered and used as intensities, being placed on an absolute scale by comparison with calculated values at a later stage of the structure determination. The intensities of an additional 266 reflections were visually estimated from unintegrated Weissenberg photographs.

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_2ZnBr_4 (Morosin & Lingafelter, 1959), and refinement of positions and individual atom isotropic temperature factors proceeded by a few Fourier sections and several difference syntheses. A final reliability index of 0·118* was obtained.

After the refinement was complete, a program for the 650 was written to introduce the dispersion corrections by the method suggested by Templeton (1955). The refinement was then continued, correcting for dispersion. The only change in atomic position was a very small shift in Cs_1 (0·008 Å). The primary effect of introducing the dispersion correction was on the temperature factors, as shown in Table 1. The reliability index changed from 0·118 to 0·117. These

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

observations are in agreement with those of Geller & Gilleo (1959).

The reliability index for special classes of reflections is as follows:

$h0l$:0·110
$h1l$:0·114
$h2l$:0·112
$h3l$:0·114
$h4l$:0·122
$h5l$:0·142

$h+l=2n$, $k=2n$:0·114
$h+l=2n$, $k=2n+1$:0·120
$h+l=2n+1$, $k=2n$:0·132
$h+l=2n+1$, $k=2n+1$:0·113

Atomic positions and individual isotropic temperature factors are listed in Table 1. All atoms are in positions (4c) except Br_3 which is in (8d). The standard deviations in the parameters, calculated according to Cruickshank (1949), are 0·004 Å for Cs, 0·007 for Cu, and 0·006 for Br.

Table 1. *Atomic positional parameters and temperature factors for* Cs_2CuBr_4

	x	y	z	$B^{(a)}$	$B^{(b)}$
Cs_1	0·1290	0·2500	0·1058	3·5	3·7
Cs_2	0·0049	0·2500	0·6694	2·8	2·95
Cu	0·2311	0·2500	0·4187	2·7	2·0
Br_1	0·0010	0·2500	0·3819	3·4	3·3
Br_2	0·3440	0·2500	0·5797	3·1	3·1
Br_3	0·2960	0·5138	0·3546	4·0	4·0

(a) Without dispersion correction.
(b) With dispersion correction.

Discussion

The crystal structure of Cs_2CuBr_4 is essentially the same as that of Cs_2CuCl_4 (Helmholtz & Kruh, 1953), consisting of Cs^+ and $CuBr_4^{-2}$ ions. Bond lengths and angles in $CuBr_4^{-2}$ are listed in Table 2 along with their standard deviations.

The observed differences in the bond lengths are probably not significant, since the maximum deviation from the mean value, 2·376 Å, is only twice the standard deviation.

Table 2. *Bond lengths and bond angles in* Cs_2CuBr_4

$CuBr_1$	2·394 ± 0·009 Å	Br_1CuBr_2	130·4 ± 0·36°
$CuBr_2$	2·380	Br_1CuBr_3	101·9 ± 0·32
$CuBr_3$	2·354	Br_2CuBr_3	99·9
		Br_3CuBr_3'	126·4
Br_1Br_2	4·333		
Br_1Br_3	3·686		
Br_2Br_3	3·624		
Br_3Br_3'	4·202		

If the distortion of $CuBr_4^{-2}$ from a regular tetrahedral configuration is due to the Jahn–Teller effect (see below), the two larger bond angles would be expected to be equal, as would the two smaller angles. However, the observed angles differ significantly, the difference between Br_1CuBr_2 and Br_3CuBr_3 being 11 times the standard deviation, while the difference between Br_1CuBr_3 and Br_2CuBr_3 is 6 times the standard deviation. Consideration of the nearest neighbor distances given in Table 3, along with the difference in the temperature factors of the two Cs^+ ions, suggests that there is steric pressure by Cs_2 on Br_3, analogous to the effect observed in the structure of Cs_2ZnBr_4 (Morosin & Lingafelter, 1959), causing an increase in the angle Br_1CuBr_3 and a decrease in Br_3CuBr_3'. If this explanation is accepted, the most probable values for the angles in the 'free' $CuBr_4^{-2}$ are 130·4° and 99·9°. However, in view of the uncertainty and complexity of such steric effects, we shall use the average angles as a basic for discussion.

Table 3. *Neighboring bromide ions*

Cs_1 at (0·6290, ¼, 0·3942)

	Type	x	y	z	Distance
1	2	0·3440	¼	0·5797	3·768 Å
2	1	0·5010	¼	0·1181	3·803
3	1	1·0010	¼	0·3819	3·796
4	3	0·7040	0·4862 0·0138	0·6454	3·832
5	2	0·6560	¾	0·4203	4·006
6	3	0·2960	0·5138 −0·0138	0·4020	3·994
7	3	0·7960	0·5138 −0·0138	0·1453	4·205
			Cs_2 at (0·5049, ¼, 0·8306)		
8	3	0·2040	0·4862 0·0138	0·8546	3·612 Å
9	2	0·3440	¼	0·5797	3·637
10	2	0·8440	¼	0·9203	3·647
11	3	0·7040	0·4862 0·0138	0·6454	3·660
12	1	0·5010	¼	1·1181	3·719
13	1	0·4990	¾	0·8819	4·038

The distortion from the regular tetrahedral configuration has now been observed for $CuCl_4^{-2}$ in Cs_2CuCl_4 (Helmholtz & Kruh, 1953) with angles of 124° and 103°,* for CuO_4 in $CuCr_2O_4$ (Prince, 1957) with angles of 123° and 103°, and for $CuBr_4^{-2}$ in Cs_2CuBr_4 with angles of 128° and 101°. The distortion has been explained by Orgel & Griffith (1957) on the basis of the Jahn–Teller effect and has been treated quantitatively by Felsenfeld (1956) for $CuCl_4^{-2}$. The increased distortion in $CuBr_4^{-2}$ compared with that in $CuCl_4^{-2}$ would appear to suggest a stronger ligand field effect (cf. Nyholm, 1956) or increased covalency (cf. Schäffer & Jørgensen, 1958).

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* These values are somewhat different from those reported by Helmholtz & Kruh (120° and 104°) and were obtained by us by extending the refinement from their $R=19·0$ to $R=10·0\%$.

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Isomerism of Benzoquinone-Monoximes (Nitrosophenols). VIII. The Crystal Structure of α-2-Chloro- and α-2-Bromo-5-Methyl-*p*-Benzoquinone-4-Oxime

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The crystals of α-2-chloro- and α-2-bromo-5-methyl-*p*-benzoquinone-4-oxime are isomorphous and monoclinic, space group $P2_1/c$. The dimensions of the unit cell of the chlorine compound are

$$a=3{\cdot}85,\ b=13{\cdot}30,\ c=14{\cdot}15\ \text{Å},\ \beta=92{\cdot}2^\circ.$$

The crystal structure of the chlorine compound has been determined by normal and generalized electron-density projections along [100]. The molecule has an oxime structure and the oxime group is *syn* with respect to the chlorine atom.

According to Kehrmann & Tichvinsky (1898) 2-chloro-5-methyl-*p*-benzoquinone-4-oxime (Cl*M*BO) and 2-bromo-5-methyl-*p*-benzoquinone-4-oxime (Br*M*BO) can be prepared in two morphologically different forms, yellow crystals (α-form) and white fibres (β-form, more soluble in solvents such as toluene). Although Hodgson & Moore (1926) did not find two forms, investigations by Umans & Talen (Umans, 1959) confirmed the results obtained by Kehrmann and established that the α- and β-forms are not—or at least not easily—interconvertible. The chemical and spectrophotometric investigations gave support to the view that the two forms might be *anti*/*syn* oxime isomers (Kehrmann & Rüst, 1898; Umans, 1959).

The behaviour of Cl*M*BO and Br*M*BO seems to be at variance with theoretical expectations. A consistent picture of the properties of quinone–monoximes had been arrived at by assuming the existence in solution of a dynamic equilibrium between quinone–monoxime and nitrosophenol molecules, interconversions occurring mainly *via* mesomeric ions (cf. Havinga & Schors, 1950, 1951). In the nitrosophenol form rotation of the NO group could be expected to occur at a non-negligible rate at room temperature. Thus in solutions of substituted quinone–monoximes interconversion of *syn*- and *anti*-isomers should take place through the equilibrium with the nitrosophenolic tautomer.

A crystallographic investigation of Cl*M*BO and Br*M*BO was deemed important since the knowledge of the shape of the molecules might prove helpful in the explanation of their rather unexpected behaviour. A preliminary communication (VI) on the structure of the α-compounds and of 3-chloro- and 3-bromo-*p*-benzoquinone-4-oxime (Romers, Brink Shoemaker & Fischmann, 1957) was published earlier. The structures of the β-compounds are discussed in this journal in paper IX of this series (Fischmann, Romers & Umans, 1960). The other reports of this series (not mentioned before) have been published elsewhere (Kraayeveld & Havinga, 1954*a*, *b*; Schors, Kraayeveld & Havinga, 1955; Romers & Umans, 1960).

Experimental part

The crystalline compounds α-Br*M*BO decomposition at 170 °C. and β-Cl*M*BO melting point 187–191 °C., prepared according to the method of Kehrmann, as described by Umans (1959), form monoclinic yellow needles with principal zone [100] and faces {010} and {102}. (102) is a perfect cleavage plane. The crystals are biaxially negatively birefringent ($n_\alpha \leqslant n_\beta < n_\gamma$) with n_α perpendicular to (102), n_β parallel to [010]

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