

Crystal Structure of Chromium(II) Bromide

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CrBr₂ crystallizes in a monoclinic unit cell, space group *C2/m*, with

$$a_0 = 7.114, b_0 = 3.649, c_0 = 6.217 \text{ \AA}; \beta = 93^\circ 53'.$$

Chromium(II) is surrounded by an elongated octahedron of bromide ions; the octahedra share their shortest edge to form infinite planar chains and longer edges to bind these chains into sandwich-like layers.

Introduction

The crystal structures of CrF₂ (Jack & Maitland, 1957), CrCl₂ (Tracy *et al.*, 1961) and CrI₂ (Tracy *et al.*, 1962) have recently been described. We now wish to report the structure of CrBr₂. The four halides have similar distorted octahedral arrangements of halogen atoms about chromium II but are each crystallographically different.

Experimental

CrBr₂ was prepared by reaction of bromine vapor with an excess of chromium metal (Fisher Scientific, 98% pure) at 700 °C.; the product was purified by fractional vacuum sublimation. Crystals suitable for X-ray examination were grown by sublimation in a silica tube in a pressure of ca. 25 cm. (Hg) of argon, with the sample held near 830 °C.; after twenty-four hours small lath-shaped prisms were found attached to the wall near the mouth of the furnace. Single crystals were mounted in Pyrex glass capillaries in a manner similar to that described in the recent papers on CrCl₂ and CrI₂ (Tracy *et al.*, 1961, 1962).

Diffraction lines from sodium chloride (a_0 taken as 5.640 Å) were superimposed on rotation and Weissenberg photographs (copper *K*α radiation, $\lambda = 1.5418$ Å) to determine the monoclinic cell dimensions:

$$a_0 = 7.114, b_0 = 3.649, c_0 = 6.217 (\pm 0.005) \text{ \AA}; \\ \beta = 93^\circ 53'.$$

Systematic absence of (*hkl*) for *h*+*k* odd, consistent with space groups *C2*, *Cm* or *C2/m*, was observed. Packing considerations and the observation that corresponding reflections on the zero and second layer lines (rotation about *b*) had similar intensities led to the choice of *C2/m*. Each cell contains the equivalent of two CrBr₂ units (calculated density, 4.370 g.cm.⁻³; observed (Biltz & Birk, 1924), 4.356 g.cm.⁻³).

A Nonius Weissenberg instrument, integrating

circumferentially only, was used to collect *h0l* intensity data. Intensities were measured with a scanning microphotometer, equipped with a logarithmic slide-wire, and were verified by visual estimation. Scanning was parallel to the axis of rotation and intensities assumed proportional to the areas under the peaks. The crystal was lath-shaped, 0.018 × 0.048 mm. (calculated optimum diameter 0.034 mm.); no correction for absorption was included. Lorentz and polarization factors were applied to obtain observed relative structure factors.

Determination of the structure

Both CrBr₂ and CrI₂ crystals show a pronounced tendency to delaminate and their Weissenberg photographs show marked similarities. However first level Weissenberg photographs of CrBr₂ could not be indexed on a pseudo-hexagonal cell like that of the iodide. A 'sandwich' layer-type trial structure with Cr in (2*a*) at 0, 0, 0, and $\frac{1}{2}, \frac{1}{2}, 0$ and *X* in (4*i*) at *x*, 0, *z*; \bar{x} , 0, \bar{z} ; $\frac{1}{2} + x, \frac{1}{2}, z$ and $\frac{1}{2} - x, \frac{1}{2}, \bar{z}$ with *x* = 0.65 and *z* = 0.24 was found satisfactory for the *h00* and *00l* reflections. A Fourier *h0l* projection and several difference syntheses (calculated on an IBM 650) led to only small shifts, and gave final values of *x* = 0.6489 and *z* = 0.2409. Individual anisotropic temperature factors, $\exp -B(\sin \theta/\lambda)^2$ with final values of

$$B_{Cr} = 1.2 + 0.7 \cos^2 (\chi - 0.195)$$

and

$$B_{Br} = 0.8 + 0.9 \cos^2 (\chi - 0.210),$$

(χ is the negative of the acute angle (cycles) between *c** and the normal to the plane), were employed to calculate structure factors. Scattering factors for Cr(II) were taken from Berghuis *et al.* (1955) and factors for bromine atoms (values for the ions were not available) from Thomas & Umeda (1957). A final reliability index of 0.105 was obtained for *h0l* data, Table 1.

A comparison of calculated *h1l* and rather rough observed structure factors, based on visually estimated

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Table 1. *Calculated and observed structure factors*
($\times 10$)

h	k	l	Obs.	Calc.	h	k	l	Obs.	Calc.
0 0	1	329	494	4 0	3	<102	-88		
0 0	2	559	-767	4 0	-4	191	-245		
0 0	3	161	139	4 0	4	384	-404		
0 0	4	1048	1044	4 0	-5	245	-266		
0 0	5	463	385	4 0	5	371	308		
0 0	6	445	-385	4 0	-6	361	391		
0 0	7	<90	-71	4 0	6	559	569		
2 0	0	83	30	4 0	-7	435	422		
2 0	-1	1584	1425	6 0	0	691	616		
2 0	1	836	-720	6 0	-1	194	-164		
2 0	-2	720	738	6 0	1	588	538		
2 0	2	506	505	6 0	-2	328	-310		
2 0	-3	464	-520	6 0	2	233	-227		
2 0	3	955	1137	6 0	-3	368	376		
2 0	-4	169	-162	6 0	3	234	-240		
2 0	4	152	166	6 0	-4	453	537		
2 0	-5	762	721	6 0	4	377	406		
2 0	5	484	-472	6 0	-5	<92	-48		
2 0	-6	515	466	6 0	5	416	438		
2 0	6	106	117	6 0	-6	254	-244		
2 0	-7	218	-237	8 0	0	249	240		
2 0	7	620	576	8 0	-1	500	461		
4 0	0	506	-432	8 0	1	206	-243		
4 0	-1	275	-252	8 0	-2	<87	3		
4 0	1	777	675	8 0	2	<75	-73		
4 0	-2	850	823	8 0	-3	199	-244		
4 0	2	979	903	8 0	3	330	383		
4 0	-3	632	698	8 0	-4	79	124		

intensities from a single unintegrated first level Weissenberg photograph (from a larger crystal) without applying corrections for absorption or distinguishing quantitatively between the most intense reflections, gave very good general correlation, although the value of R was rather large, 0.27. A series of calculations with bromine atom positions fixed and chromium atoms moved progressively along the y axis (possible if the space group were $C2$ instead of $C2/m$) showed R to have its minimum value with the chromium atoms at the origin (and $\frac{1}{2}, \frac{1}{2}, 0$). Hence

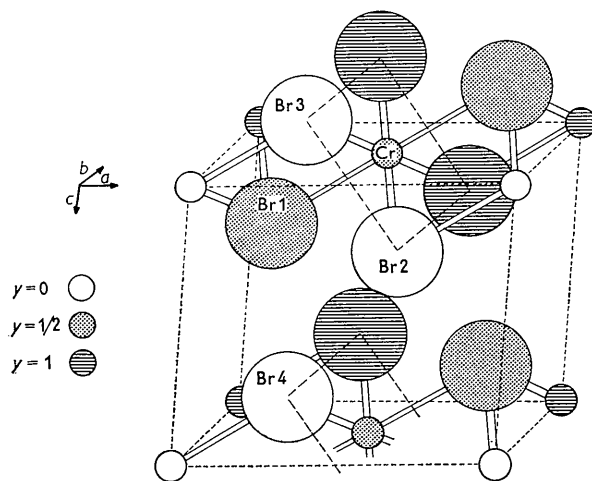


Fig. 1. Crystal structure of CrBr_2 . Large circles, bromine; small circles, chromium.

the structure deduced from the space group $C2/m$ and $h0l$ data has been assumed correct.

Interatomic distances, with probable errors as indicated by Cruickshank's criteria (1949), are given in Table 2 (numbers refer to Fig. 1).

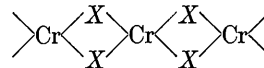
Table 2. *Interatomic distances and bond angles*

Cr-Br(1)	$2.998 \pm 0.01 \text{ \AA}$
Cr-Br(2)	2.545
Br(1)-Br(2)	3.998
Br(1)-Br(3)	3.867
Br(1)-Br(4)	3.892
Br(2)-Br(3)	3.549
Br(2)-Br(4)	3.974
Br(1)-Cr-Br(3)	$88.1^\circ \pm 0.4^\circ$
Br(2)-Cr-Br(3)	$88.4^\circ \pm 0.4^\circ$

Discussion

Each chromium ion is at the center of a slightly irregular plane of four bromide ions at 2.54 Å with two others on a line nearly perpendicular to the plane at 3.00 Å. Each halogen is shared by three chromium ions and each chromium by six halogens. The distorted CrBr_6 octahedra are linked, sharing their shortest edge, to form densely packed planar 'ribbons' parallel to the b axis; they also share four long edges, forming a 'sandwich' layer structure. The close proximity of z to $\frac{1}{4}$ shows that the mean distance between the layers of halogens is nearly the same, even though metal ions are all in the 001 planes. The shortest (Br-Br) interlayer distance (3.892 Å) and the shortest (Br-Br) distance across the sandwich (3.549 Å) are both less than the diameter usually assigned to the bromide ion, 3.92 Å.

The structures and bond distances of the four chromium(II) halides are compared in Fig. 2 and Table 3. All show an elongated octahedral coordination of the halogens with slight deviation from regularity in the plane of ions surrounding the chromium ion. The fluoride is unique with two slightly different short Cr-F distances. The four short Cr-X distances are equivalent in each of the other structures. The octahedral groups share edges in the monoclinic fluoride and the orthorhombic chloride in a similar way. The packing along the planar 'ribbons' of



is very dense in the chloride, bromide and iodide where the unit cell dimension in this direction corresponds to a halogen atom diameter less than the usual assigned value. The packing in the fluoride is not as 'tight' in this direction; c_0 for the fluoride and chloride are virtually identical.

CrBr_2 and CrI_2 have the same space group and differ only in the manner in which the sandwich layers are packed. The iodide structure gives a more favorable arrangement for interaction of the halide

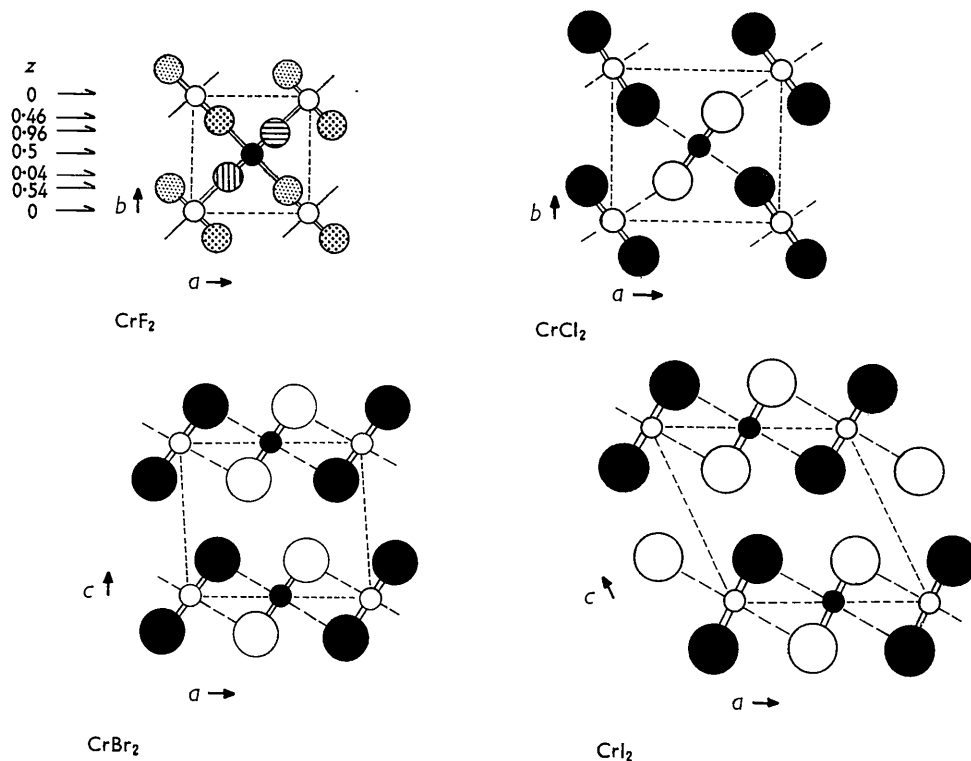


Fig. 2. Comparison of structures of CrF_2 , CrCl_2 , CrBr_2 , CrI_2 . Small circles, Cr; large circles X; open circles, y (or z) = 0; black circles, y (or z) = $\frac{1}{2}$, except for CrF_2 where z values are indicated.

Table 3. Bond lengths and apparent radius of the chromium(II) ion

	CrF_2 (Å)	CrCl_2 (Å)	CrBr_2 (Å)	CrI_2 (Å)
Short Cr-X bond	1.98 2.01	2.39	2.54	2.74
Long Cr-X bond	2.43	2.92	3.00	3.24
Difference	0.43	0.53	0.46	0.50
Ratio	0.82	0.82	0.85	0.85
*X ⁻ ion radius	1.36	1.75	1.82	1.96
Apparent Cr(II) ion radius				
Short	0.64	0.64	0.72	0.78
Long	1.07	1.17	1.18	1.28

* F^- from Pauling (1960); the Cl^- radius is taken as $c_0/2$; $b_0/2$ for Br^- and I^- . These values are smaller than usually quoted (Pauling, 1960) but seem appropriate for CrX_2 crystals.

ions of one sandwich with the chromium ions of a neighbor. The greater polarizability of the larger iodide ion may explain why the two structures are different.

The data in Table 3 show a reasonable progression of bond lengths and a virtually constant ratio of the long and short bond distances in the four compounds. The short bonds in CrF_2 and CrCl_2 indicate a chromium(II) radius of 0.64. A slightly larger value is

possible in CrBr_2 and CrI_2 , which is to be expected as a result of the larger size of the heavier halogen atoms.

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