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Cubic Structure of Chromium–Bromine Boracite at 298 and 113 K

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Abstract

$Cr_3B_7O_{13}Br$, $M_r = 519.55$, cubic, $F\bar{4}3c$, $Z = 8$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $F(000) = 1968$. At 298 K: $a = 12.1524\ (1)$ Å, $V = 1794.68\ (3)$ Å^3, $D_x = 3.845$ Mg m^{-3}, $\mu = 8.533$ mm^{-1}, final $R = 0.020$ for 206 unique reflections with $I > 3\sigma(I)$; shortest interatomic distances (Å): Cr—O = 2.061 (2), Cr—Br = 3.03810 (3), B—O = 1.436 (3), O—O = 2.388 (2). At 113 K: $a = 12.1340\ (3)$ Å, $V = 1786.54\ (13)$ Å^3, $D_x = 3.863$ Mg m^{-3}, $\mu = 8.533$ mm^{-1}, final $R = 0.025$ for 281 unique reflections with $I > 3\sigma(I)$; shortest interatomic distances (Å): Cr—O = 2.057 (2), Cr—Br = 3.0335 (1), B—O = 1.436 (3), O—O = 2.390 (2). The planarity of the metal-centred CrO_4 groups does not differ significantly from that in other chromium-based cubic boracites and generally increases as the temperature is lowered.

Introduction

So far the cubic phases of seven boracites $M_3B_7O_{13}X$ (M = bivalent metal ion, X = halogen ion) based on 3*d* transition elements, M = Cr, Co, Ni, Cu, have been structurally characterized [for a review see Nelmes (1974); for later work see Monnier, Berset, Schmid & Yvon (1987), and references therein]. The metal ions in these structures are tightly bound to four nearly planar oxygen atoms and loosely bound to two apical halogen atoms. Most boracites (hereafter *M-X*) undergo structural phase transitions to non-cubic low-temperature modifications in which all (or part) of the metal ions strongly attract one of the halogen ligands. The known transition temperatures are situated between 60 K (Ni-I; Schmid, 1965) and 797 K (Cd-Cl; Schmid & Tippmann, 1978). With a view to investigating the factors responsible for this large temperature range we have decided to study cubic $Cr_3B_7O_{13}Br$ (hereafter Cr-Br). This compound together with Cr-I and Cu-I make up the exceptional and sole boracite compositions for which no structural transition to a non-cubic phase occurs down to very low temperature. This has been verified by observation in polarized light down to 10 K for Cr-Br and Cr-I (Schmid, 1965), reconfirmed for Cr-Br down to 9 K (Ye, 1991), and down to 15 K for Cu-I (Monnier *et al.*, 1987).

Experimental

Blue cube-shaped Cr-Br crystals were grown by the chemical vapour transport method (Schmid, 1965). Data collection: CAD-4 automatic four-circle diffractometer, graphite monochromator, liquid-

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å$^2 \times 10^4$) *at* 298 K (*first line*) *and* 113 K (*second line*)

U_{eq} = 1/3trace$U$, space group $F\bar{4}3c$, e.s.d.'s in parentheses.

		x	y	z	U_{eq}
Cr	24(*c*)	0	2500	2500	81 (3)
		0	2500	2500	42 (3)
Br	8(*b*)	2500	2500	2500	120 (1)
		2500	2500	2500	59 (1)
B(1)	24(*d*)	2500	0	0	43 (19)
		2500	0	0	18 (16)
B(2)	32(*e*)	798 (2)	798 (2)	798 (2)	83 (7)
		797 (2)	797 (2)	797 (2)	47 (6)
O(1)	8(*a*)	0	0	0	83 (8)
		0	0	0	39 (6)
O(2)	96(*h*)	196 (1)	968 (1)	1800 (1)	61 (11)
		190 (1)	969 (1)	1798 (1)	39 (12)

Table 2. *Interatomic distances* (Å) *and deviation from planarity*, ε (Å), *of the metal-centred* CrO_4 *groups in cubic* Cr-X (X = *halogen*) *boracites, with e.s.d.'s in parentheses*

	Cr-Cl*	Cr-Br†		Cr-I‡
	291 K	298 K	113 K	298 K
Cr—O(2)	2.055 (2)	2.061 (2)	2.057 (2)	2.075 (2)
Cr—X	3.033 (1)	3.03810 (3)	3.0335 (1)	3.0520 (2)
O(2)—O(2)§	2.389 (2)	2.388 (2)	2.390 (2)	2.393 (3)
B(2)—O(2)	1.436 (3)	1.436 (3)	1.436 (3)	1.439 (3)
B(1)—O(2)	1.465 (1)	1.471 (2)	1.470 (2)	1.479 (2)
B(2)—O(1)	1.683 (2)	1.679 (2)	1.676 (2)	1.682 (2)
ε	0.241 (1)	0.238 (1)	0.231 (1)	0.238 (2)

* Nelmes & Thornley (1974).
† This work.
‡ Monnier, Berset, Schmid & Yvon (1987).
§ Shortest contact distance.

Table 3. *Anisotropic displacement parameters* (Å^2) *of metal ions in cubic boracites*

$\langle u^2\rangle_{\parallel}$ ($\langle u^2\rangle_{\perp}$): directions parallel (perpendicular) to metal–halogen bonds.

	$\langle u^2\rangle_{\perp}$	$\langle u^2\rangle_{\parallel}$	$\langle u^2\rangle_{\parallel}/\langle u^2\rangle_{\perp}$	Ref.
Cr-Cl (291 K)	0.0043 (2)	0.0218 (3)	5.1 (3)	(1)
Cr-Br (298 K)	0.0047 (1)	0.0151 (3)	3.2 (1)	(2)
Cr-Br (113 K)	0.0027 (1)	0.0073 (2)	2.7 (2)	(2)
Cr-I (298 K)	0.0040 (3)	0.0109 (3)	2.7 (3)	(3)
Ni-I (293 K)	0.0070 (2)	0.0219 (3)	3.1 (1)	(4)
Ni-I (77 K)	0.0022 (5)	0.0110 (7)	5.0 (1.2)	(5)

References: (1) Nelmes & Thornley (1974); (2) this work; (3) Monnier, Berset, Schmid & Yvon (1987); (4) Nelmes & Thornley (1976); (5) Thornley, Kennedy & Nelmes (1976).

nitrogen cooling device (Enraf–Nonius, Delft), measuring temperatures 298 and 113 K, crystal size 0.07 mm edge length, one hemisphere ($-16 \le h, k \le 16$), $(\sin\theta/\lambda)_{max} = 0.799$ Å^{-1}; 2116 (298 K), 2960 (113 K) integrated intensities, θ–2θ scans, two standard reflections; maximum intensity change 2.0% (298 K), 1.3% (113 K), spherical absorption correction ($\mu R = 0.30$), lattice parameters determined from 60 (298 K) and 24 (113 K) reflections with $57.5 < 2\theta < 64.7°$ (298 K) and $51.8 < 2\theta < 52°$ (113 K); structure refinement by full-matrix least squares, function minimized $\sum w(|F_o| - |F_c|)^2$, unit weights; scattering factors for neutral atoms and anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974, Vol. IV), 22 parameters refined [one scale factor, four positional parameters, fourteen anisotropic and one overall displacement parameters, one extinction parameter and one absolute structure parameter (Flack, 1983)], using the *XTAL*3.0 program system (Hall & Stewart, 1990). Residuals at 298 K: R (wR) = 0.020 (0.019), for 206 contributing reflections; residuals at 113 K: R (wR) = 0.025 (0.018), for 281 contributing reflections; $(\Delta/\sigma)_{max}$ = 0.011 (298 K), 0.0035 (113 K). The refined values for the absolute structure parameter were 1.02 (3) at 298 K and 0.97 (3) at 113 K.

The atomic parameters are listed in Table 1,* a comparison of bond lengths for chromium-based boracite structures is given in Table 2, and a comparison of anisotropic displacement parameters of the metal atoms in cubic boracites is given in Table 3.

Results and discussion

The chromium atoms in Cr-Br are coordinated by four close oxygen atoms in a nearly square-planar configuration, and by two distant apical halogen atoms (Fig. 1). The bond distances, Cr—O = 2.061 (2), Cr—Br = 3.03810 (3) Å at room temperature, are intermediate between those of Cr-Cl and Cr-I (Table 2). They increase as a function of ionic size of the halogens and decrease as the temperature is decreased. By comparison, the boron–oxygen bond distances and oxygen–oxygen contact distances change only little, thus confirming the picture of a relatively rigid oxygen–boron network.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54612 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

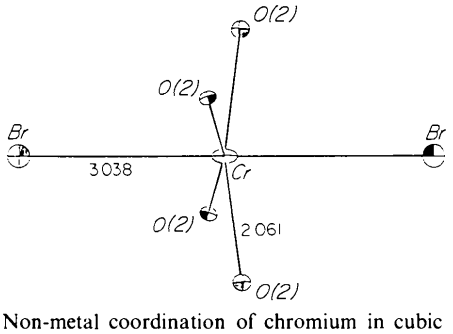

Fig. 1. Non-metal coordination of chromium in cubic Cr-Br at 298 K. Thermal ellipsoids are drawn at 50% probability scale. Distances in Å.

As expected from the topology of the boracite structure and its bonding, the metal ions vibrate mainly along the fourfold axis *i.e.* in directions parallel to the weak metal–halogen bonds and perpendicular to the strong metal–oxygen bonds. Within the chromium-based series the anisotropy of the displacement amplitudes is largest for Cr-Cl, $\langle u^2\rangle_{\parallel}/\langle u^2\rangle_{\perp} \simeq 5.1$ (Table 3). It decreases with increase of the ionic size of the halogens but does not vary significantly as a function of temperature. There is also no significant difference between the temperature dependence of the displacement amplitudes in a boracite that is structurally stable such as Cr-Br and in one that is structurally unstable such as Ni-I (T_1 = 60 K).

The deviation from planarity of the CrO_4 groups in Cr-Br, ε, does not differ significantly from that in the other chromium-based boarcites Cr-Cl and Cr-I, but decreases as the temperature is lowered. This is surprising in view of the overall trend of ε that increases with the cubic cell parameter, a, as suggested by Monnier *et al.* (1987), and illustrated in Fig. 2. Notice that for a given temperature a does not always correlate with the size of the halogens, as can be seen, for example, with the copper-based boracites Cu-Br and Cu-I. These observations can be taken as further evidence for the contribution of the transition element to the complex atomic interactions in boracites. For example, Jahn–Teller-active ions such as Cu^{2+} (d^9) and Cr^{2+} (d^4) could contribute to preserve a square-planar oxygen environment around the transition metal. This could decrease the tendency toward a structural phase transition and explain the absence of such a transition in Cr-Br, Cr-I and Cu-I. In other boracites this transition usually changes the square-planar metal coordination to a square-pyramidal one. Theoretical calculations and further structural data are necessary to confirm this hypothesis.

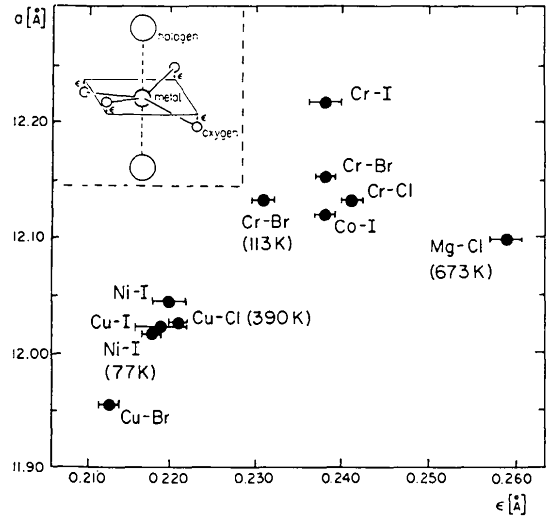

Fig. 2. Deviation from planarity, ε (for definition see insert), of the O-atom environment around the metal atoms (site symmetry of metal atoms $\bar{4}$) in cubic boracites as a function of cell parameter, a. Data include Cr-Cl (Nelmes & Thornley, 1974), Cr-I (Monnier, Berset, Schmid & Yvon, 1987), Co-I (Nelmes & Hay, 1981), Ni-I (T = 293 K, Nelmes & Thornley, 1976; T = 77 K, Thornley, Kennedy & Nelmes, 1976), Cu-Cl (Thornley, Nelmes & Kennedy, 1976), Cu-Br (Nelmes & Hay, 1981), Cu-I (Berset, Depmeier, Boutellier & Schmid, 1985), Mg-Cl (T = 673 K, Sueno, Clark, Papike, & Konnert, 1973), Cr-Br (T = 298 K, 113 K, this work). Except for Cu-Cl (T = 390 K), Ni-I (T = 77 K), Mg-Cl (T = 673 K), and Cr-Br (T = 113 K), all data refer to room temperature. Error bars: ± 1 e.s.d.

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