two-dimensional polymerization, due to the *trans* position of the two tridentate borohydrates, confirms the structure suggested by Charpin *et al.* (1978) from an X-ray powder pattern of $U(BH_4)_4$ II.

The six B atoms form a distorted octahedron of *mm* symmetry around the U atom. The four B atoms of the bidentate borohydrides [B(1)] are coplanar and lie in the symmetry plane (001) (at $z = \frac{1}{4}$ and $\frac{3}{4}$), as do two of their H atoms, H(11) and H(12), and the U atom; the two B atoms of the tridentate borohydrides [B(2)] are located in the perpendicular symmetry plane (100). The B(2)—U—B(2) axis deviates considerably from linearity [162·9 (5)°]: this distortion may result from the packing requirement for H atoms around the U atom, as has been pointed out by Bernstein, Keiderling, Lippard & Mayerle (1972).

The U—H distances of the bidentate BH_4^- vary from 2·1 (1) to 2·7 (1) Å. The terminal H(23) atom of the tridentate ligand is oriented away from the U atom with a U—B—H(23) angle of 162 (6)°. Although the H-atom positions were not refined, the deviation by 18° from linearity seems significant: this bending renders inequivalent the three bridging H atoms and brings two of them closer to the U atom [U—H(22) 2·23 (8) Å], the third H(21) being rejected at 2·8 (1) Å. Such a geometry for the BH_4 bonding may be considered as an intermediate solution between bi- and tridentate bonding. An idealized geometry for the tridentate bonding would require the three U—H distances to be 2·34 Å [$U(BH_4)_4$ form I (Bernstein, Hamilton, Keiderling, La Placa, Lippard & Mayerle, 1972)], the terminal U—B—H being 180°, whereas in bidentate bonding the two H atoms would be at 2·45 Å from the U atom. This particular positioning of the tridentate BH_4 ligand has not so far been found in other uranium borohydrides, except in $[U(BH_4)_4(OC_4H_8)_2]$ (Charpin, Nierlich, Vigner, Lance & Baudry, 1987) and $[U(BH_4)_4\{OP(C_6H_5)_3\}_2]$ (Charpin, Nierlich, Chevrier, Vigner, Lance & Baudry, 1987).

In both forms of $U(BH_4)_4$, four bidentate and two tridentate borohydrides give the same coordination number of 14 H atoms around each U atom. Both structures are of polymeric type: they only differ by the distribution of bidentate and tridentate groups leading to a three- or two-dimensional network.

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Structure of Hashemite, $Ba(Cr,S)O_4$

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Abstract. $M_r = 250·1$, orthorhombic, *Pnma*, $a = 9·113$ (2), $b = 5·536$ (1), $c = 7·340$ (2) Å, $V = 370·3$ (1) Å^3, $Z = 4$, $D_x = 4·46$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 123·09$ cm^{-1}, $F(000) = 442·02$, $T = 293$ K, $R = 0·053$ for 541 unique reflections. Hashemite is isostructural with baryte, with Cr substituting for S in the tetrahedral site. The refined site occupancy is 84% Cr and 16% S. The average *T*—O bond length is 1·657 Å and the average O—*T*—O bond angle is 109·4°. The mean Ba—O distance is 2·966 Å. Ba is twelve-coordinated. O(1) and O(2), which lie on an (010) mirror plane, have large U_{22} thermal parameters.

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Introduction. The first occurrence of hashemite, $Ba(Cr,S)O_4$, was reported by Hauff, Foord, Rosenblum & Hakki (1983), who found it in veinlets of a phosphatic carbonate rock, 60 km SE of Amman, Jordan.

A crystal of hashemite was found during routine identification of a sample collected in the same locality described by Hauff *et al.* (1983). In this sample hashemite occurs as brown tabular prismatic crystals, and is associated with Cr-ettringite, calcite and bultfonteinite (P. Orlandi, 1986, personal communication). The EDS (energy dispersive spectrometer) analysis of the mineral showed strong Ba and Cr peaks, and a much weaker peak for S. The following unit-cell parameters were refined through least-squares cycles from Gandolfi measurements: $a = 9{\cdot}121$ (3), $b = 5{\cdot}523$ (3), $c = 7{\cdot}319$ (3) Å.

The structure refinement of hashemite was carried out to confirm its isostructurality with baryte, and to determine the extent of sulfur–chromium substitution in the tetrahedral site and the consequences of this substitution on the tetrahedral bond lengths and angles.

Experimental. A prismatic, euhedral crystal was selected for single-crystal structure analysis, dimensions *ca* 0·8 × 0·8 × 0·2 mm. Weissenberg photographs showed Laue symmetry and systematic absences consistent with space groups *Pnma* and $Pn2_1a$. Ital Structures four-circle automatic diffractometer, 22 reflections ($22 \leq \theta \leq 24°$) used for determination of unit-cell dimensions, absorption correction following North, Phillips & Mathews (1968) (transmission-factor range 0·99–1·28). 1261 reflections measured with $3 \leq \theta \leq 30°$, h −12 to 12, k 0 to 7, l 0 to 10, θ–2θ scan, reflection 040 monitored every hundredth reflection, intensity variation 5·2%, 541 unique reflections with $I \geq 2\sigma(I)$, $R_{\text{int}} = 0{\cdot}068$ and 0·033 before and after absorption correction, respectively. Structure refined on F in the centrosymmetric space group *Pnma* to $R = 0{\cdot}053$, $wR = 0{\cdot}050$ $\{w = 1/[\sigma(F_o)]^2\}$, anisotropic thermal parameters for all the atoms, scattering factors from *International Tables for X-ray Crystallography* (1974) with corrections for real and imaginary parts of anomalous dispersion. The structure was solved and refined using the *SHELX76* set of programs (Sheldrick, 1976); the e.s.d.'s on bond distances and angles were computed using *PARST* (Nardelli, 1983);* max. $\Delta/\sigma = 0{\cdot}24$; max. and min. heights in the final difference Fourier synthesis 3·0 and −2·9 e Å^{-3}.

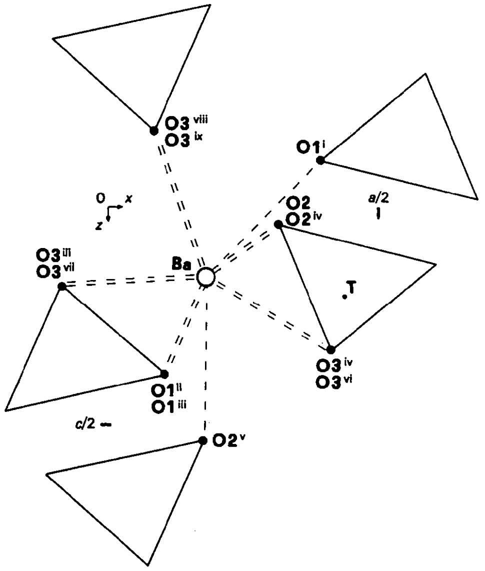

Fig. 1. The crystal structure of hashemite, as viewed down **b**.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å²) *for hashemite*

$$B_{\text{eq}} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	B_{eq}
Ba	0·1831 (1)	$\frac{1}{4}$	0·1554 (2)	0·86
T*	0·4422 (3)	$\frac{3}{4}$	0·1945 (4)	0·57
O(1)	0·6109 (14)	$\frac{3}{4}$	0·1152 (20)	1·64
O(2)	0·3160 (19)	$\frac{3}{4}$	0·0328 (21)	3·17
O(3)	0·4172 (10)	0·9942 (15)	0·3233 (12)	0·93

* The T site is occupied by 84% Cr and 16% S.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for hashemite*

T—O(1)	1·644 (13)		Ba—O(1^{i})	2·733 (13)
—O(2)	1·652 (16)		—O(1^{ii})	3·306 (8)
—O(3)	1·665 (8)		—O(1^{iii})	3·306 (8)
—O(3^{vi})	1·665 (8)		—O(2^{v})	2·770 (15)
Average value	1·657		—O(2)	3·152 (8)
	O···O	O—T—O	—O(2^{iv})	3·152 (8)
	distance	angle	—O(3^{iii})	2·811 (9)
			—O(3^{vii})	2·811 (9)
O(1)—O(2)	2·754 (21)	113·4 (7)	—O(3^{iv})	2·841 (8)
O(1)—O(3) (×2)	2·697 (14)	109·2 (3)	—O(3^{vi})	2·841 (8)
O(2)—O(3) (×2)	2·688 (16)	108·2 (3)	—O(3^{viii})	2·933 (9)
O(3)—O(3)	2·704 (11)	108·5 (3)	—O(3^{ix})	2·933 (9)
Average value	2·705	109·4	Average value	2·966

Symmetry code: (i) $1-x, 1-y, -z$; (ii) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (iii) $x-\frac{1}{2}, y-1, \frac{1}{2}-z$; (iv) $x, y-1, z$; (v) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (vi) $x, \frac{3}{2}-y, z$; (vii) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}-z$; (viii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (ix) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$.

Discussion. The crystal structure of hashemite is depicted in Fig. 1. Fractional atomic coordinates and B_{eq} thermal parameters are reported in Table 1. Selected bond distances and bond angles are reported in Table 2. It has been confirmed, as expected, that hashemite is the isostructural, Cr-dominant counterpart of baryte. To make comparison easier, the same asymmetric unit of the last refinement of baryte (Hill, 1977) was chosen.

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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 43944 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ba is twelve-coordinated, and this implies that every O atom is linked to three Ba atoms and one T atom, giving it fourfold coordination. In Table 2 the twelve Ba—O distances, which range from 2·73 to 3·31 Å, are reported, in keeping with the statement of Hill (1977) that all of them are significant in the electrostatic valence balance. In a previous refinement of baryte Colville & Staudhammer (1967) set a somewhat arbitrary limit between nearest and next-nearest neighbouring O atoms.

As regards the (Cr,S) tetrahedron, the resulting site occupancy (Cr 84%, S 16%) is intermediate between the compositions given by Hauff *et al.* (1983) for a dark and a zoned crystal of hashemite (93 and 77% Cr, respectively); our composition seems quite reasonable, if one considers the dark appearance of the crystal, which indicates a Cr-rich variety of hashemite. The Cr/S ratio was calculated from the refined average T—O bond length of 1·651 Å (as obtained from the first least-squares cycles, in which the occupancy of the T site was allowed to vary) through linear interpolation of the theoretical Cr—O and S—O distances, 1·68 and 1·50 Å respectively, assuming 1·38 Å as the ionic radius of the four-coordinate O^{2-} species (Shannon & Prewitt, 1969). In the last cycles of refinement the occupancy of the T site was held fixed.

The O(1) and O(2) atoms display large U_{22} thermal parameters, *i.e.* major vibration in the direction perpendicular to the mirror plane on which O(1) and O(2) lie; Hill (1977) noticed the same phenomenon during his refinement of baryte, and ascribed this behaviour to the weaker bonding of O(1) and O(2) by Ba cations. In hashemite a further cause of the anomalous thermal vibration may be found in the statistical occupancy of the tetrahedral site by different cations, with consequent variations in the O positions.

We wish to thank P. Orlandi for supplying the hashemite crystal and providing information about its paragenesis; S. Merlino is thanked for a thoughtful reading of the manuscript and for many useful suggestions.

Note added in proof: After this paper had been sent to the press we discovered that an independent refinement had been carried out by Duesler & Foord [*Am. Mineral.* (1986), **71**, 1217–1220]. The structural results are in close agreement.

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Aluminophosphate Number 5: Time-of-Flight Neutron Powder Diffraction Study of Calcined Powder at 295 K

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Abstract. Aluminium phosphate, $AlPO_4$, $M_r = 121·95$, hexagonal, $P6cc$ for ordered Al and P but refined in $P6/mcc$ for disordered Al, P, $a = 13·7707$ (3), $c = 8·3789$ (6) Å, $V = 1376·0$ (2) Å^3, $Z = 12$, $D_x = 1·76$ g cm^{-3}, range of wavelengths from time-of-flight pulsed neutron technique, $T \sim 295$ K, $R_p = 1·9$% for $d = 0·865$–$3·308$ Å and 396 allowed Bragg reflections. Significant non-crystalline scattering was observed and successfully removed. Refinement in space group $P6/mcc$ resulted in T—O distances ranging from 1·56 to 1·64 Å and T—O—T angles from 143 to 176°. Attempts to refine the ordered structure in $P6cc$ were not entirely successful. The sample was obtained by calcination of as-synthesized $(AlPO_4)_{12}$–tetrapropylammonium hydroxide (1/2). Removal of tetrapropylammonium hydroxide from the as-synthesized material results in 0·3% expansion of a, 1·2% contraction of c,

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