Crystal structure of hashemite, BaCrO₄, a barite structure type

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ABSTRACT

The crystal structure of hashemite, naturally occurring $Ba(Cr,S)O_4$, a 9.1028(14), b 5.5276(7), c 7.3314(11) Å, Z = 4, space group *Pnma,* has been refined by least-squares methods to $R = 0.0479$ ($R_w = 0.0447$) using 815 graphite-monochromatized MoKα reflections. Distortion of the CrO_4 tetrahedron, as indicated by the significantly higher equivalent isotropic temperature factors for O(1) and O(2) relative to O(3), is analogous to that of the SO_4 tetrahedron in barite. This is attributed to slight disorder of the atoms from their ideal positions.

INTRODUCTION

Hashemite, the naturally occurring chromate analogue of barite, was described by Hauff et al. (1983). Although the crystal structure of barite is well known and has been recently further refined by Hill (1977) and Miyake et al. (1978), the structure of synthetic or natural $BaCrO_4$ has not been fully determined. Only X-ray powder-diffraction data and thermal expansion properties of the synthetic material have been published by Jellinek (1960) and Pistorius and Pistorius (1962). In order to compare the structures of hashemite and barite, the crystal structure of hashemite has been determined.

Crystallographic data and structure refinements were obtained from a single composite crystal of hashemite, having the average composition $Ba(Cr_{0.90}S_{0.10})_{\Sigma1.00}O_4$ as determined by electron-microprobe analysis. A crystal $0.092 \times 0.138 \times 0.207$ mm was used for data collection. The θ-2θ X-ray profiles of this fragment showed a width at half-maximum of approximately 0.62° 2θ. Although there were no discernible double maxima, a smaller shoulder could be seen on the high-angle side of the profiles of the reflections examined (210, 020, and 002). The crystallographic data are given in Table 1.

EXPERIMENTAL PROCEDURE

Intensity data were collected using a Nicolet P3/F automated four-circle diffractometer equipped with a graphite monochromator and using MoKα radiation ($\lambda = 0.71069$ Å) for reflections in the $h,k,\pm l$ and $-h,-k,\pm l$ quadrants. Data-collection parameters are given in Table 2. Three standard relections were monitored after every 141 reflections collected. The data were corrected for Lorentz and polarization effects, redundant data were averaged, and space group extinct reflections were removed. Absorption coefficients were obtained from Volume IV of the *International Tables for X-ray Crystallography* (1974). An empirical absorption correction was made using an ellipsoidal model fitted to the intensities of azimuthal scans and then applied to the intensity data. The residuals for the agreement of the azimuthal scan intensities before and after application of the absorption correction are 9.36% and 1.94%, respectively. The residual for the averaging of the sets of four equivalent $|F|_o$ values collected was 2.16%.

All computations and Figure 1 were done with the SHELXTL crystallographic package (Sheldrick, 1981).

Table 1. Crystallographic data for hashemite

$F(000) = 448$
Space group = *Pnma* (no. 62)
Formula units/unit cell (Z) = 4
Density (measured) = 4.54 g·cm⁻³
Density (calculated) = 4.52 g·cm⁻³
μ (MoKα) = 133.51 cm⁻¹

Note: Cell parameters obtained by least-squares fit to the settings for 25 reflections, in the range 11.12° < 2θ < 52.34°. $a = 9.1028(14)$ Å, $b = 5.5276(7)$ Å, $c = 7.3314(11)$ Å; $\alpha = \beta = \gamma = 90.00(0)°$; $V = 368.9(1)$ Å³.

Table 2. θ-2θ data collection parameters

Data collection temperature: 18(2)°C
Scan range: 1.3° below 2$\theta(K\alpha_1)$ to 1.4° above 2$\theta(K\alpha_2)$
Scan speed: 4–30 deg·min⁻¹
Total background counting time/total scan time = 0.5
2θ limits; 1 < h, $k \pm l$, 70°, also Friedel related reflections
Three standards collected every 141 reflections: 511, 040, 006
Absorption correction based on azimuthal scans:
  R before correction = 9.36%;
  R after correction = 1.94%
Maximum and minimum transmissions: 0.025/0.002
3694 reflections collected
881 unique, space-group–allowed reflections
815 reflections with $F > 6$ $\sigma(F)$
R for merging equivalent reflections = 2.16%
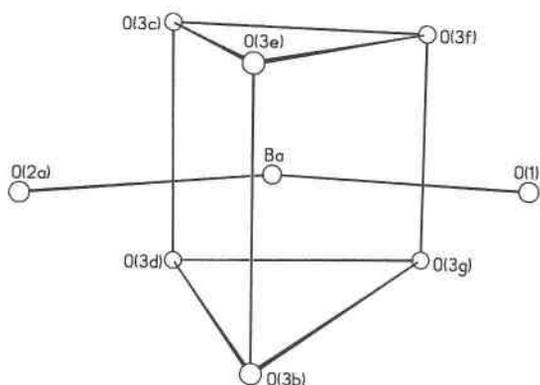
Fig. 1.   Oxygen coordination polyhedron about barium.

structure determination of barite as starting positions for Ba and Cr (Hill, 1977). These positions were consistent with a sharpened Patterson map obtained from the present data. Phasing using these atoms yielded the expected Fourier map. Agreement with all atoms isotropically refined was $R = 0.0805$.

Final residual factors after 20 cycles of refinement are $R = \Sigma\|F|_o - |F|_c\|/\Sigma|F|_o = 0.0479$, $R_w = [\Sigma w(|F|_o - |F|_c)^2/\Sigma w|F|_o^2]^{1/2} = 0.0447$ and $w = 1/(\sigma^2(F) + |g|F^2)$, where $g = 0.00076$. Structure factor amplitudes are given in Table 3.[1] For the final cycle, the maximum least-squares shift/error was 0.0001 for x/c of Ba. The final difference map showed a maximum of 2.92 e/Å³ and a minimum of -2.40 e/Å³.

Blocked-cascade least-squares with full-matrix blocks of as many as 103 parameters were refined on F, using anomalous dispersion factors for all atoms. Neutral-atom atomic scattering factors and anomalous dispersion factors were taken from Volume IV of the *International Tables for X-ray Crystallography* (1974). All derivatives were calculated analytically. Estimated standard deviations (e.s.d.'s) in bond lengths and angles were derived from the diagonal elements of the inverse matrix used in the last cycle of refinement.

The structure solution of hashemite was begun using the Ba and S locations found in the previously published

DISCUSSION

The structure consists of discrete CrO_4 anions and Ba cations. The oxygen coordination polyhedron about the Ba cation is a bi-capped trigonal prism, the two trigonal end faces being formed by O(3)b, O(3)d, O(3)g and O(3)c, O(3)e, O(3)f, respectively. The O(1) atom caps the face formed by O(3)b, O(3)e, O(3)f, and O(3)g. The O(2)a atom
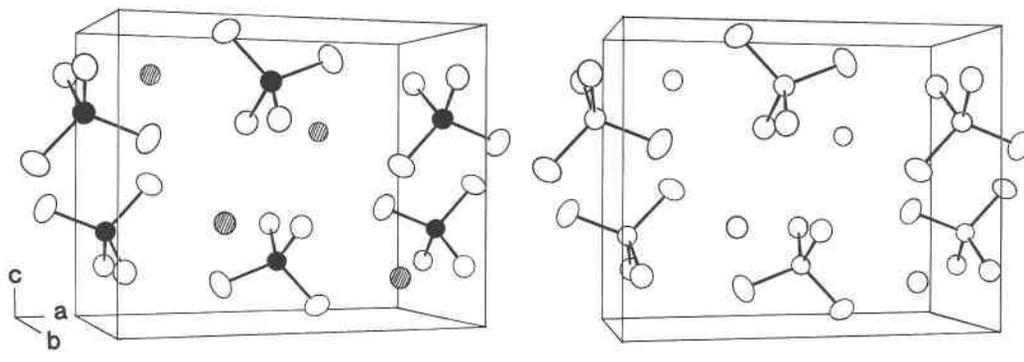
Fig. 2a.   ORTEP stereo pair of hashemite. Rotation axis = c. Lined spheres = Ba atoms, solid spheres = Cr atoms, and open spheres = oxygen atoms.
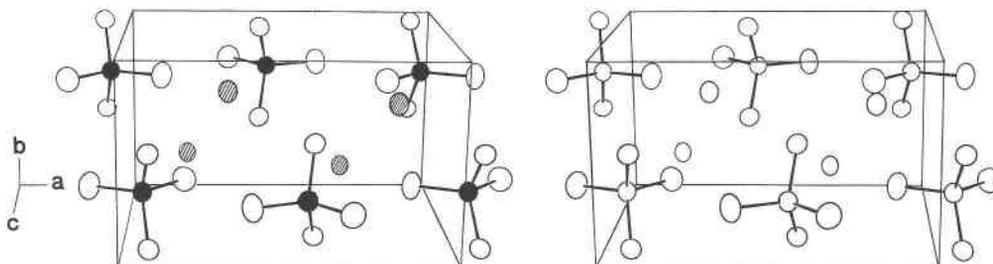
Fig. 2b.   ORTEP stereo pair of hashemite. Rotation axis = b. Lined spheres = Ba atoms, solid spheres = Cr atoms, and open spheres = oxygen atoms.

Table 4. Anisotropic temperature factors (Å²) for hashemite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	0.0242(2)	0.0348(2)	0.0259(2)	0	−0.0003(1)	0
Cr	0.0245(4)	0.0275(4)	0.0240(4)	0	0.0004(3)	0
O(1)	0.031(2)	0.056(3)	0.048(3)	0	0.013(2)	0
O(2)	0.043(3)	0.048(3)	0.032(2)	0	−0.009(2)	0
O(3)	0.031(1)	0.028(1)	0.034(1)	0.002(1)	−0.001(1)	0.000(1)

Note: The anisotropic-temperature-factor exponent takes the form $-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2(U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Table 5. Atomic coordinates and equivalent isotropic temperature factors for hashemite

Atom	x/a	y/b	z/c	U_{equiv} (Å²)
Ba	0.81690(3)	3/4	−0.15551(5)	0.0283(1)
Cr	0.44225(9)	3/4	0.19404(13)	0.0253(2)
O(1)	0.6099(6)	3/4	0.1146(10)	0.045(2)
O(2)	0.3185(5)	3/4	0.0330(9)	0.041(2)
O(3)	0.4180(3)	0.5078(7)	0.3231(5)	0.031(1)

caps the face formed by O(3)b, O(3)d, O(3)c, and O(3)e (Fig. 1).

The diagonal terms of the thermal coefficients for Ba and oxygen are on the average 2.0–2.5 times larger in hashemite than in barite (Hill, 1977). This could be the result of either disorder in the crystal or the lower quality of the hashemite crystal. The U_{22} parameters of Ba, Cr, and to a lesser degree of O(1) and O(2) are greater than the other U_{ii} terms (Table 4). Hill (1977) also reported this situation for barite. He suggested that a slight deviation of these atoms from the symmetry plane could account for the large U_{22} terms and also the distortion of the SO₄ unit from the expected tetrahedral symmetry.

Atomic coordinates and equivalent isotropic U values for hashemite are given in Table 5. Bond lengths and bond angles are given in Table 6. The hashemite structure also displays a distorted CrO₄ tetrahedron (Table 6). It seems likely that the type of disorder found in barite may also be in effect here. An attempt was also made to refine hashemite in $Pn2_1a$. It was hoped that freeing the atoms on the mirror plane would mitigate the temperature-factor problem. However, refinement in the noncentric space group did not improve the residual, and the polyhedra became even more distorted.

Figure 2 shows ORTEP stereoscopic projection pairs (Johnson, 1965) of the hashemite structure in the ac plane and the ab plane.

Table 6. Bond lengths (Å) and angles (°) for hashemite

Ba–O(1)	2.733(7)	O(2)a–Ba–O(3)e	64.7(1)
Ba–O(2)a	2.768(7)	O(2)a–Ba–O(3)f	146.1(1)
Ba–O(3)b	2.849(3)	O(2)a–Ba–O(3)g	146.1(1)
Ba–O(3)c	2.807(3)	O(3)b–Ba–O(3)c	151.1(1)
Ba–O(3)d	2.807(3)	O(3)b–Ba–O(3)d	111.5(1)
Ba–O(3)e	2.849(3)	O(3)b–Ba–O(3)e	60.0(1)
Ba–O(3)f	2.929(3)	O(3)b–Ba–O(3)f	145.4(1)
Ba–O(3)g	2.929(3)	O(3)b–Ba–O(3)g	111.5(1)
		O(3)c–Ba–O(3)d	61.0(1)
		O(1)–Cr–O(2)	112.8(3)
Cr–O(1)	1.634(6)	O(1)–Cr–O(3)	109.2(2)
Cr–O(2)	1.632(6)	O(2)–Cr–O(3)	108.8(2)
Cr–O(3)	1.654(4)	O(1)–Cr–O(3h)	109.2(2)
Cr–O(3h)	1.654(4)	O(2)–Cr–O(3h)	108.8(2)
O(2)–Ba(i)	2.768(4)	O(3)–Cr–O(3h)	108.1(2)
		Ba–O(1)–Cr	154.4(4)
O(2)a–Ba–O(3)d	86.5(1)	Cr–O(2)–Ba(i)	136.6(3)
O(1)–Ba–O(2)a	136.7(2)	O(3)c–Ba–O(3)e	111.5(1)
O(1)–Ba–O(3)b	78.2(1)	O(3)c–Ba–O(3)f	62.9(1)
O(1)–Ba–O(3)c	129.3(1)	O(3)c–Ba–O(3)g	90.5(1)
O(1)–Ba–O(3)d	129.3(1)	O(3)d–Ba–O(3)e	151.1(1)
O(1)–Ba–O(3)e	78.2(1)	O(3)d–Ba–O(3)f	90.5(1)
O(1)–Ba–O(3)f	67.3(1)	O(3)d–Ba–O(3)g	62.9(1)
O(1)–Ba–O(3)g	67.3(1)	O(3)e–Ba–O(3)f	111.5(1)
O(2)a–Ba–O(3)b	64.7(1)	O(3)e–Ba–O(3)g	145.4(1)
O(2)a–Ba–O(3)c	86.5(1)	O(3)f–Ba–O(3)g	54.5(1)

Note: Symmetry operations applied:
a $0.5 + x, 1.5 - y, -0.5 - z$
b $1 - x, 1 - y, -z$
c $1.5 - x, 0.5 + y, -0.5 + z$
d $1.5 - x, 1 - y, -0.5 + z$
e $1 - x, 0.5 + y, -z$
f $0.5 + x, 1.5 - y, 0.5 - z$
g $0.5 + x, y, 0.5 - z$
h $x, 1.5 - y, z$
i $-0.5 + x, 1.5 - y, -0.5 - z$

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