

Fig. 1. Polyhedral representations drawn with *STRUPLO* (Fischer, 1985) of the (a) monoclinic and (b) tetragonal polymorphs of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Unit-cell edges are indicated by the heavy lines, and heights of the cations central to each polyhedron are given in hundredths of the cell repeat in the projection direction.

positional parameters of non-H atoms do not differ significantly from those reported here, but Gerkin & Reppart were unable to refine the positions of the H atoms. Their smaller reported unit-cell parameters have resulted in shorter bond distances.

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Structure of Barium Perchlorate Trihydrate

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Abstract. $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, $M_r = 390.28$, hexagonal, $P6_3/m$, $a = 7.277(2)$, $c = 9.656(1) \text{ \AA}$, $V = 442.9(1) \text{ \AA}^3$, $Z = 2$, $F(000) = 368$, $D_x = 2.93 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $T = 295 \text{ K}$, $\mu = 52.60 \text{ cm}^{-1}$, 456 unique reflections, $R = 0.023$. The barium atoms in this structure are coordinated by six water oxygens, O(3), at $2.919(1) \text{ \AA}$ and by six perchlorate oxygens, O(2), at $3.026(2) \text{ \AA}$ in a slightly distorted icosahedral

The readers attention is also drawn to the recent determination of the absolute configuration of $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ by Stadnicka, Glazer & Koralewski [*Acta Cryst.* (1988), **B44**, 356–361].

References

- BARGOUTH, M. O. & WILL, G. (1981). *Int. Cent. Theor. Phys. Rep.* pp. 1–9.
- BAUR, W. H. (1962). *Acta Cryst.* **15**, 815–826.
- BAUR, W. H. (1964). *Acta Cryst.* **17**, 1361–1369.
- BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147.
- BEEVERS, C. A. & LIPSON, H. (1932). *Z. Kristallogr.* **83**, 123–135.
- BURNHAM, C. W. (1966). *Am. Mineral.* **51**, 159–167.
- COTTON, F. A., FALVELLO, L. R., LLUSAR, R., LIBBY, E., MURILLO, C. A. & SCHWOTZER, W. (1986). *Inorg. Chem.* **25**, 3423–3428.
- ELERMAN, Y. (1988). *Acta Cryst.* **C44**, 599–601.
- FINGER, L. W. & PRINCE, E. (1974). *A System of Fortran IV Computer Programs for Crystal Structure Computations*. Natl Bur. Stand. (US) Tech. Note 854.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
- FUESS, H. (1970). *Z. Anorg. Allg. Chem.* **379**, 204–212.
- GROTH, P. (1908). *Chem. Kristallogr.* **2**, 423–428.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- O'CONNOR, B. H. & DALE, D. H. (1966). *Acta Cryst.* **21**, 705–709.
- PALMER, R. A., GILES, H. F. & GROSS, P. M. (1978). *J. Chem. Soc. Dalton Trans.* pp. 977–980.
- PTASIEWICZ-BAK, H., MCINTYRE, G. J. & OLOVSSON, I. (1983). *Acta Cryst.* **C39**, 966–968.
- SNYMAN, H. C. & PISTORIUS, C. W. F. T. (1964). *Z. Kristallogr.* **119**, 465–467.
- STADNICKA, K., GLAZER, A. M. & KORALEWSKI, M. (1987). *Acta Cryst.* **B43**, 319–325.
- STEELE, B. D. & JOHNSON, F. M. G. (1904). *J. Chem. Soc.* **85**, 116.
- SUTOR, D. J. (1959). *Acta Cryst.* **12**, 72.
- ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1962). *Acta Cryst.* **15**, 1219–1224.
- ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1964). *Acta Cryst.* **17**, 235–240.

[O(2)] perchlorate oxygen is hydrogen bonded to two water molecules; thus each perchlorate ion is hydrogen bonded to nine water molecules. Conversely, each water molecule [O(3)] oxygen is hydrogen bonded to six perchlorate ions – to two through axial [O(1)] oxygens and to four through trigonal [O(2)] oxygens.

Introduction. Through our interest in the structure of barium perbromate trihydrate (Gerkin, Reppart & Appelman, 1988) we became interested in the structure of barium perchlorate trihydrate. In a previous report on the structure of barium perchlorate trihydrate, Mani & Ramaseshan (1960) were unable to decide definitely on the basis of their data whether the space group was $P6_3$ or $P6_3/m$, although their discussion of the structure was based upon the $P6_3$ assignment. We hoped to be able to resolve this question of the space-group assignment as well as to obtain a more fully characterized structure, and thus undertook the study reported here.

Experimental. Crystals of barium perchlorate trihydrate were produced by slow evaporation at room temperature from a barium perchlorate solution formed from G. F. Smith reagent barium perchlorate trihydrate and $\sim 1 M$ perchloric acid. A clear, colorless crystal in the form of a doubly capped, short hexagonal column having eighteen faces and principal dimensions $\sim 0.15 \times \sim 0.15 \times \sim 0.31$ mm was analyzed at 295 K with a Rigaku AFC5S diffractometer, utilizing graphite-monochromated Mo $K\alpha$ radiation.

Unit-cell parameters were obtained from a least-squares fitting of the setting angles for 25 well centered reflections with $20 \leq 2\theta \leq 30^\circ$. Intensity data were measured for 1114 reflections with $+h$, $+k$, $+l$ and $-h$, $-k$, $-l$ indices ($h_{\max} = 8$; $k_{\max} = 8$; $l_{\max} = 13$), and 2θ values in the range $4 \leq 2\theta \leq 60^\circ$. The ω - 2θ scan technique was employed with scan widths $(1.30 + 0.35 \tan\theta)^\circ$ in ω , and a background/scan time ratio of 0.5. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections ($\bar{1}\bar{1}0$; $0\bar{1}\bar{2}$; 230 ; 410 ; $31\bar{4}$; 106) were measured after every 150 reflections, and while $\bar{1}\bar{1}0$ exhibited a slight intensity increase over the course of the data collection, the remaining five standards showed a maximum relative intensity variation of $\pm 2.8\%$. Accordingly, no decay correction was applied. The data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied using the program of de Meulenaer & Tompa (1965) and Alcock (1970).

The space groups $P6_3$ and $P6_3/m$ were allowed, based on the observed systematic absences ($00l$, $l = \text{odd}$). No Bijvoet differences were observed, however, which favored assignment of the space group as

Table 1. Final atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) for barium perchlorate trihydrate, with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}[U_{33} + \frac{2}{3}(U_{11} + U_{22} - U_{12})].$$

	x	y	z	U_{eq}
Ba	0	0	0	227 (2)
Cl	$\frac{1}{2}$	$\frac{1}{2}$	0.03411 (9)	189 (3)
O(1)	$\frac{1}{2}$	$\frac{1}{2}$	-0.1132 (3)	274 (9)
O(2)	0.1811 (3)	0.4592 (3)	0.0838 (2)	353 (6)
O(3)	0.2562 (4)	0.1686 (4)	$\frac{1}{4}$	261 (8)
H(1)	0.361 (10)	0.160 (9)	$\frac{1}{4}$	910 (214)
H(2)	0.310 (6)	0.326 (6)	$\frac{1}{4}$	365 (113)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for barium perchlorate trihydrate; e.s.d.'s are given in parentheses

Coordination polyhedron			
Ba—O(2)	3.026 (2)	O(3 ⁱⁱ)—O(2)—O(3)	56.53 (9)
Ba—O(3)	2.919 (1)	O(2 ⁱⁱⁱ)—O(2)—O(3)	67.02 (4)
		O(3 ⁱⁱⁱ)—O(2)—O(2 ^v)	65.32 (4)
O(2)—O(3)	2.916 (3)	O(2 ⁱⁱⁱ)—O(2)—O(3 ^v)	53.80 (6)
O(2)—O(3 ⁱⁱ)	3.080 (3)	O(2 ^v)—O(2)—O(3 ^v)	50.71 (6)
O(2)—O(2 ⁱⁱⁱ)	3.334 (3)		
O(2)—O(3 ^v)	3.468 (2)	O(3 ⁱⁱⁱ)—O(3)—O(2)	64.66 (9)
O(3)—O(3 ⁱⁱ)	2.843 (4)	O(2 ⁱⁱⁱ)—O(3)—O(2)	62.27 (4)
		O(3 ⁱⁱⁱ)—O(3)—O(3 ^v)	60
		O(2 ⁱⁱⁱ)—O(3)—O(2 ^v)	60.88 (4)
		O(3 ^v)—O(3)—O(2 ^v)	58.81 (9)
Water molecule			
O(3)—H(1)	0.79 (5)	H(1)—O(3)—H(2)	104 (5)
O(3)—H(2)	1.01 (4)		
Perchlorate ion			
Cl—O(1)	1.423 (3)	O(1)—Cl—O(2)	109.50 (8)
Cl—O(2)	1.437 (2)	O(2)—Cl—O(2 ⁱ)	109.45 (8)
O(1)—O(2)	2.335 (3)		
O(2)—O(2 ⁱ)	2.346 (3)		
Hydrogen bonds			
O(3)—O(1 ^{vi})	2.920 (2)	O(3)—H(1)—O(1 ^{vi})	130 (3)
O(3)—O(1 ^{vii})	2.920 (2)	O(3)—H(1)—O(1 ^{vii})	130 (3)
O(3)—O(2 ^{iv})	3.080 (3)	O(3)—H(1)—O(2 ^{iv})	107 (4)
O(3)—O(2 ^{viii})	3.080 (3)	O(3)—H(1)—O(2 ^{viii})	107 (4)
O(3)—O(2)	2.916 (3)	O(3)—H(2)—O(2)	118 (2)
O(3)—O(2 ^{ix})	2.916 (3)	O(3)—H(2)—O(2 ^{ix})	118 (2)
O(3)—O(1 ^v)	2.920 (2)	O(3)—H(2)—O(1 ^v)	82 (2)
O(3)—O(1 ^{vii})	2.920 (2)	O(3)—H(2)—O(1 ^{vii})	82 (2)

Code for symmetry-related atoms: (none) x, y, z ; (i) $1-y, x-y+1, z$; (ii) $-y, x-y, z$; (iii) $y, y-x, -z$; (iv) $y-x, -x, z$; (v) $x-y, x, -z$; (vi) $1-x, 1-y, \frac{1}{2}+z$; (vii) $1-x, 1-y, -z$; (viii) $y-x, -x, \frac{1}{2}-z$; (ix) $x, y, \frac{1}{2}-z$.

$P6_3/m$. Nonetheless, the special locations of the heavier atoms (Ba, Cl) and some of the O atoms brought into question whether the observed absence of Bijvoet differences is a secure basis for excluding $P6_3$ as an allowed space-group assignment for this structure. Accordingly, both the $P6_3/m$ and the $P6_3$ assignment were tested. Although the minimum R value achieved for the $P6_3$ assignment was virtually identical to that for the $P6_3/m$ assignment, the five-times-larger number of correlation coefficients of magnitude greater than 0.5 (and ranging up to 0.94), and the near satisfaction of special relations among certain coordinates that would be exactly satisfied under $P6_3/m$ led to the definite

conclusion that the $P6_3$ assignment is untenable. Hence $P6_3/m$ was established and adopted as the space group for this structure. Averaging of equivalent reflections gave 458 independent observations, with $R_{\text{int}} = 0.016$. The positions of the barium and chlorine atoms were assigned from a Patterson map, and the oxygen atoms and hydrogen atoms were subsequently located using Fourier methods. Full-matrix least-squares refinement was performed using the *TEXSAN* (Molecular Structure Corporation, 1987) structure analysis package to minimize the function $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$, in which $\sigma_F = \sigma_f/2FLp$, for the unique reflections. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for Ba, Cl and O; scattering factors for H were taken from Stewart, Davidson & Simpson (1965).

Initially, the unique reflections with $I > 3\sigma$ were included in the calculations; in the later stages, two reflections (002 and 110) showing secondary extinction were rejected and all other unique reflections with $I > 0$ were included. The hydrogen atoms, which were located from Fourier difference maps, had their coordinates and isotropic thermal parameters refined by least-squares methods.

The results for the final refinement cycle were: 456 independent observations; 30 variables; $R = 0.023$; $wR = 0.028$; $S = 1.4$; $(\Delta/\sigma)_{\text{max}} = 0.01$.^{*} Maximum and minimum peaks on the final electron density difference map had values $+0.49$ and $-0.91 \text{ e } \text{Å}^{-3}$, respectively. The maximum peak was located at $x = 0.42$, $y = 0.69$, $z = -0.24$, $\sim 1.4 \text{ Å}$ from each of two O(1) atoms; the minimum peak was located at $x = 0.63$, $y = 0.30$, $z = 0.51$, $\sim 0.4 \text{ Å}$ from a Cl atom.

The final atomic coordinates and equivalent isotropic thermal parameters and their uncertainties are given in Table 1. Interatomic distances and angles of particular interest are given in Table 2 together with their uncertainties.

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51194 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The barium atoms in this structure are coordinated by twelve oxygen atoms, six perchlorate ion O(2) atoms at 3.026 Å distance and six water molecule O(3) atoms at 2.919 Å distance, which form the apices of a slightly distorted icosahedron. Columns of these icosahedra are centered on the 6_3 axis passing through the unit-cell origin, with successive icosahedra sharing a common face formed by three O(3) atoms. The separate columns of coordinated barium atoms are linked through the perchlorate ions, each of which participates *via* its O(2) atoms in three different icosahedra. A stereoview of the structure is shown in Fig. 1.

Consistent with the initial location and subsequent least-squares refinement of the H(1) and H(2) atom positions at $z = \frac{1}{4}$, the water molecules were found to lie in planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. The subsequent delineation of hydrogen bonds (see Table 2) showed that each water molecule O(3) atom is hydrogen-bonded to two axial [O(1)] perchlorate oxygens at 2.920 Å distance through both H(1) and H(2), and to four trigonal [O(2)] perchlorate oxygens, two at 2.916 Å distance through H(2) and two others at 3.080 Å distance through H(1). Thus, each water molecule participates in hydrogen bonding to six perchlorate groups. Conversely, each axial [O(1)] perchlorate oxygen is hydrogen-bonded to three water molecules and each trigonal [O(2)] perchlorate oxygen is hydrogen-bonded to two water molecules; each perchlorate ion is thus hydrogen-bonded to nine water molecules.

The perchlorate ion in this salt fails by a narrow margin to exhibit regular tetrahedral symmetry to within the experimental error. In view of the involvement of the trigonal perchlorate [O(2)] oxygen atoms both in the barium-centered icosahedra and in hydrogen bonds with water and of the involvement of the axial perchlorate [O(1)] oxygen atoms only in hydrogen bonds with water, a slight distortion should perhaps be expected. The average Cl—O bond length, $1.433 (6) \text{ Å}$, is well within the normal range and may be compared, for example, to the value 1.436 Å for $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (Chomnilpan, Liminga & Tellgren, 1977) or to the value 1.426 Å found for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Berglund, Thomas & Tellgren, 1975).

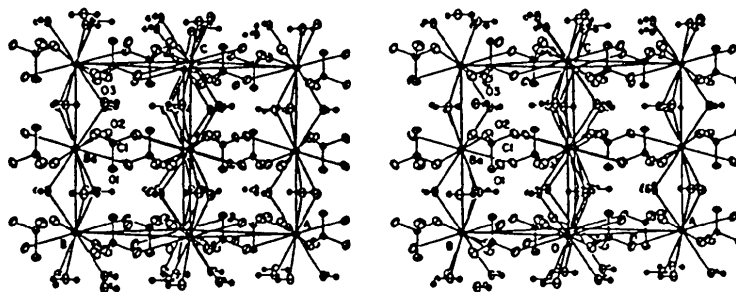


Fig. 1. An ORTEPII (Johnson, 1971) stereoview of a portion of the barium perchlorate trihydrate structure. Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

The previous ambiguity in the space-group assignment has been resolved, the centrosymmetric assignment $P6_3/m$ being quite definite. Thus the space-group assignment for barium perbromate trihydrate [which was tested in the same manner as described above for the perchlorate and with the same results (private communication, R. E. Gerkin)] is indeed the same as that for barium perchlorate trihydrate, as surmised previously by Gerkin, Reppart & Appelman (1988).

Although in general terms the structure presented by Mani & Ramaseshan (1960) is in good accord with the present determination, there are numerous differences in detail. Since the previous description was based on photographic observations of 152 unique reflections and the final R value achieved was 0.22, the present description entirely supersedes it with respect to quantitative details.

On the basis of the present results it appears most likely that the water molecule H atoms in the $\text{Ba}(\text{BrO}_4)_2 \cdot 3\text{H}_2\text{O}$ structure also lie entirely in the planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ rather than out of the plane as surmised by Gerkin, Reppart & Appelman (1988). Indeed, re-examination of the final electron density difference map for that structure revealed a peak at $x = 0.32$, $y = 0.31$, $z = \frac{1}{4}$ of appropriate magnitude for an H atom and approximately 1 Å from O(3). This is particularly suggestive since H(2) as assigned here in the perchlorate should appear in the perbromate at $x = 0.305$, $y = 0.320$, $z = \frac{1}{4}$. Since no second corresponding peak was observed in the difference list, however, no

least-squares refinement of H-atom positions in the perbromate has been pursued.

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References

- ALCOCK, N. W. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, pp. 271–278. Copenhagen: Munksgaard.
- BERGLUND, B., THOMAS, J. O. & TELLGREN, R. (1975). *Acta Cryst.* **B31**, 1842–1846.
- CHOMNILPAN, S., LIMINGA, R. & TELLGREN, R. (1977). *Acta Cryst.* **B33**, 3954–3957.
- CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- GERKIN, R. E., REPPART, W. J. & APPELMAN, E. H. (1988). *Acta Cryst.* **C44**, 960–962.
- JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- MANI, N. V. & RAMASESHAN, S. (1960). *Z. Kristallogr.* **114**, 200–214.
- MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Molecular Structure Corporation (1987). *TEXSAN. Structure Analysis Package*, version 2.1. Molecular Structure Corporation, College Station, Texas, USA.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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Structure of Bis[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]copper(II)

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Abstract. $[\text{Cu}(\text{C}_{15}\text{H}_{22}\text{BN}_6)_2]$, $M_r = 658.03$, triclinic, $P1$, $a = 10.201$ (1), $b = 10.875$ (1), $c = 8.787$ (1) Å,

$\alpha = 83.68$ (1), $\beta = 101.62$ (1), $\gamma = 117.59$ (1)°, $V = 846.1$ (2) Å³, $D_x = 1.30$ g cm⁻³, $Z = 1$, $T = 298$ K, $F(000) = 347$, $\mu(\text{Cu } K\alpha) = 11.04$ cm⁻¹, $\lambda = 1.5418$ Å, $R = 0.052$ for 2285 observed reflections. The copper

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