

Table 2. Distances (Å) and angles (°) in the NbO₆ octahedron and in the PO₄ tetrahedron

Nb	O(1)	O(1 ⁱ)	O(1 ⁱⁱ)	O(2)	O(2 ⁱ)	O(2 ⁱⁱ)
O(1)	1.994 (4)	2.792 (8)	2.792 (8)	2.786 (7)	3.961 (9)	2.798 (7)
O(1 ⁱ)	88.9 (2)	1.994 (4)	2.792 (8)	2.786 (7)	3.961 (9)	2.798 (7)
O(1 ⁱⁱ)	88.9 (2)	88.9 (2)	1.994 (4)	3.961 (9)	2.798 (7)	2.786 (7)
O(2)	89.4 (2)	89.9 (2)	177.9 (2)	1.968 (4)	2.828 (9)	2.828 (9)
O(2 ⁱ)	177.9 (2)	89.4 (2)	89.9 (2)	91.8 (2)	1.968 (4)	2.828 (9)
O(2 ⁱⁱ)	89.9 (2)	177.9 (2)	89.4 (2)	91.8 (2)	1.968 (4)	2.828 (9)

P	O(1)	O(1 ⁱⁱⁱ)	O(2 ^{iv})	O(2 ^v)
O(1)	1.516 (4)	2.501 (9)	2.494 (6)	2.461 (5)
O(1 ⁱⁱⁱ)	111.2 (4)	1.516 (4)	2.461 (5)	2.494 (6)
O(2 ^{iv})	110.3 (3)	108.1 (3)	1.525 (4)	2.481 (9)
O(2 ^v)	108.1 (3)	110.3 (3)	108.9 (4)	1.525 (4)

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

The NbO₆ octahedra are regular as shown from the O—O distances (Table 2) but the niobium atom is off-center in its octahedron by about 0.04 Å along *c*, leading to two sets of Nb—O distances significantly different at 3σ.

Since only one independent site is available for niobium, a statistical distribution of Nb^V and Nb^{IV} on the octahedral sites can be proposed. This oxide, which is the first Nasicon phosphate involving the lone

mixed-valence Nb^V—Nb^{IV}, is characterized by a high Nb^{IV} content, *i.e.* 50%. The possibility of introducing alkali ions or alkaline-earth ions in the cages in order to increase the Nb^V/Nb^{IV} ratio will be investigated. The study of the local environment of niobium by EPR is in progress.

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The Structures of Thallous Perbromate at 294 and 169 K

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Abstract. TlBrO₄, *M_r* = 348.28, orthorhombic, *Pnma*, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ Å}$, *Z* = 4, *F*(000) = 592; *T* = 294 K, *a* = 9.182 (2), *b* = 6.095 (2), *c* = 7.649 (2) Å, *V* = 428.1 (2) Å³, *D_x* = 5.40 g cm⁻³, $\mu = 472.21 \text{ cm}^{-1}$, 764 unique reflections with *I* > 0, *R* = 0.073, *wR* = 0.050; *T* = 169 K, *a* = 9.140 (1), *b* = 6.049 (1), *c* = 7.612 (1) Å, *V* = 420.9 (1) Å³, *D_x* = 5.50 g cm⁻³, $\mu = 480.31 \text{ cm}^{-1}$, 628 unique reflections with *I* > 0, *R* = 0.072, *wR* = 0.071. These structures are of the BaSO₄ type and consist of nearly regular tetrahedral perbromate ions and monovalent thallium ions coordinated in an irregular geometry by ten O atoms from seven perbromate groups. The mean Br—O bond lengths were found to be 1.603 (6) Å at 294 K and

1.609 (9) Å at 169 K and are in good agreement with previous values; the mean O—Br—O bond angles were 109.4 (2)° at 294 K and 109.4 (3)° at 169 K. The principal departure of the perbromate ions from regular tetrahedral geometry is angular. Attempted refinement in the potential alternative space group *Pna*2₁ failed.

Introduction. Through an initial interest in crystalline lanthanide perbromates, we have become interested in the structures of other simple perbromates. We have previously reported on the structure of barium perbromate trihydrate (Gerkin, Reppart & Appelman, 1988) and of nickel perbromate hexahydrate (Gallucci, Gerkin & Reppart, 1988). We here report structural studies of monovalent thallium perbromate.

Experimental. Crystals of thallous perbromate were produced by slow evaporation at room temperature

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from a thallos perbromate solution formed by the reaction of thallos carbonate (Aldrich Gold Label) with a slight excess of dilute aqueous perbromic acid, prepared by the method described by Appelman (1972)*. Clear colorless crystals with approximate principal dimensions $0.28 \times 0.32 \times 0.32$ mm (294 K study) and $0.16 \times 0.16 \times 0.30$ mm (169 K study) were selected. Each crystal had eight faces: (210), ($2\bar{1}0$), (001) and (101) with their Friedel pairs (294 K study); (101), ($10\bar{1}$), (210) and (211) with their Friedel pairs (169 K study). They were analyzed with a Syntex P1 diffractometer with an LT1 low-temperature attachment, utilizing graphite-monochromated Mo $K\alpha$ radiation. Temperature measurements were made at the cold-stream exit nozzle during data collection and at the crystal site after data collection with a Fluke 2100A digital thermometer (Type K thermocouple).

At room temperature (294 K), unit-cell parameters were obtained from a least-squares fit of the setting angles for 25 well centred reflections with $20 < 2\theta < 30^\circ$. Intensity data were measured for 945 reflections (excluding the standards) with $+h$, $+k$, $+l$ indices ($h_{\max} = 13$, $k_{\max} = 9$, $l_{\max} = 11$) and 2θ values in the range $4 \leq 2\theta \leq 65^\circ$. The ω - 2θ scan technique was employed with scan widths from $2\theta(\text{Mo } K\alpha_1) - 1.0^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 1.1^\circ$ and a background/scan time ratio of 0.5. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = R^2(C+4B) + (0.02I)^2$, where R is the variable scan rate, C is the total number of counts, B is the total number of background counts, and I is the integrated intensity [$I = R(C-2B)$]. Six standard reflections (122, 210, 301, 421, 513, 611) were measured after every 94 reflections. The intensity variations of the standards were non-systematic and were less than 5.8% of the respective average intensities; accordingly, no decay correction was applied. Transmission factors ranged from 0.002 to 0.030. 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).

At low temperature (169 K; estimated uncertainty ± 2 K), unit-cell parameters were obtained from a least-squares fit of the setting angles for 25 well centred reflections with indices identical to those used for the room-temperature study. Intensity data were measured for 760 reflections (excluding the standards) with $+h$, $+k$, $+l$ indices ($h_{\max} = 12$, $k_{\max} = 8$, $l_{\max} = 10$) and 2θ values in the range $4 \leq 2\theta \leq 60^\circ$. Six standard reflections (230, 042, 133, 124, 314, 104) were measured after every 100 reflections. The intensity variations of the standards were non-systematic and were less than 6.3% of the respective average intensities; accordingly,

no decay correction was applied. Transmission factors ranged from 0.014 to 0.057. In the remaining aspects, the procedures were identical to those given above for the room-temperature study.

Analysis and refinement. Consistent with the observed values of the cell parameters and observed symmetries in reflection intensities, the unit cell was determined to be orthorhombic. The observed extinctions ($0kl$, $k+l = \text{odd}$; and $hk0$, $h = \text{odd}$) then permitted only two space groups: the non-centrosymmetric group $Pna2_1$ (No. 33) (in the non-standard setting $Pn2_1a$) and the centrosymmetric group $Pnma$ (No. 62). Although Bössem & Herrmann (1928) reported that the monovalent perchlorates NH_4ClO_4 , KClO_4 , RbClO_4 , CsClO_4 and TlClO_4 are isomorphic and gave the space group as $Pnma$, they did not discuss the possibility of assigning it as $Pna2_1$. Subsequently, Siegel, Tani & Appelman (1969) considered both of these space groups in analyzing the structure of potassium perbromate. Although they adopted the centrosymmetric choice, their analysis did not rule out the non-centrosymmetric possibility. For these reasons and also because we did not wish to assume that TlClO_4 and TlBrO_4 (or KBrO_4 and TlBrO_4) must necessarily be assignable to the same space group, both possible assignments were tested using our room-temperature data. Whereas least-squares refinement proceeded well in $Pnma$, no satisfactory refinement was obtained in $Pna2_1$; indeed, characteristic effects of improper imposition of a non-centrosymmetric assignment (such as very near satisfaction of relations among certain coordinates which if satisfied exactly would accommodate the higher symmetry assignment) were consistently observed in the latter case. Thus $Pnma$ is strongly indicated as the room-temperature space group for TlBrO_4 . [Similarly, Tutov, Gavrilov, Isupov, Kolycheva & Fundamenskii (1986) have strongly supported the space-group assignment for NH_4BrO_4 as $Pnma$.] The very close correspondence of the 169 K data to the room-temperature data made it clear that no phase transition had occurred and $Pnma$ was thus established for the 169 K structure also.

For the room-temperature structure solution, the initial locations of Tl and Br were obtained from a Patterson map. The O positions were then obtained one by one from subsequent electron density difference maps. Four of the five atoms are located on a mirror plane. Full-matrix least-squares refinement was performed using the *SHELX76* program (Sheldrick, 1976) to minimize the function $\sum \sigma_F^{-2}(|F_o| - |F_c|)^2$, in which $\sigma_F = \sigma_f/2FLp$, for the 770 unique reflections with $I > 0$. Neutral-atom scattering factors for Tl and for Br were taken from Cromer & Waber (1965), and the O-atom scattering factor was taken from Cromer & Mann (1968). Correction for anomalous dispersion was included for Tl and for Br atoms (Cromer & Liberman, 1970).

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The results for the final refinement cycle were: 764 independent observations (six reflections showing extinction and for which the difference between $|F_o|$ and $|F_c|$ was greater than $5\sigma_F$ prior to the final refinement cycle were excluded from the final cycle); 34 variables; $R = 0.073$; $wR = 0.050$; $w = 1/\sigma^2(F)$; $S = 1.5$; $(\Delta/\sigma)_{\max} < 0.01$; $\Delta\rho_{\max} = +3.7$; $\Delta\rho_{\min} = -4.1 \text{ e } \text{\AA}^{-3}$. The maximum density difference peak was located $\sim 1.6 \text{ \AA}$ from Tl while the minimum peak was located $\sim 0.8 \text{ \AA}$ from Br. A typical value of the final electron density difference close to the heavy atoms was $\sim 2 \text{ e } \text{\AA}^{-3}$. The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* Interatomic distances and angles calculated using the *XRAY* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) are given in Table 2.

Initial atom locations for the 169 K structure were taken from the room-temperature structure. Otherwise, the procedures were identical to those described above for the room-temperature structure solution and were carried out on the 631 unique reflections with $I > 0$. The results for the final refinement cycle were: 628 independent observations (three reflections showing extinction and for which the difference between $|F_o|$ and $|F_c|$ was greater than $5\sigma_F$ prior to the final cycle were excluded from the final cycle); 34 variables; $R = 0.072$; $wR = 0.071$; $w = 1/\sigma^2(F)$; $S = 3.0$; $(\Delta/\sigma)_{\max} < 0.01$; $\Delta\rho_{\max} = +4.3$; $\Delta\rho_{\min} = -7.9 \text{ e } \text{\AA}^{-3}$. The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. Interatomic distances and angles calculated using the *XRAY* system are given in Table 2.

Discussion. The TlBrO_4 structures are of the BaSO_4 type as described by Wyckoff (1963), as are also those of KClO_4 , RbClO_4 , CsClO_4 , NH_4ClO_4 and TiClO_4 as assigned by Bössem & Herrmann (1928), and KBrO_4 (Siegel, Tani & Appelmann, 1969) and NH_4BrO_4 (Tutov, Gavrilov, Isupov, Kolycheva & Fundamenskii, 1986).

As illustrated in detail in Fig. 1, the TlBrO_4 structures consist of nearly regular tetrahedral perbromate ions and thallous ions which are coordinated in an irregular geometry by ten oxygens from seven perbromate ions.

At 294 K, the perbromate Br—O bond lengths range from 1.598(10) to 1.612(15) Å with a mean value of 1.603(6) Å, while the O—Br—O angles range from 107.4(4) to 113.8(8)° with a mean value of 109.4(2)° (Table 2). Thus, while the mean Br—O bond length agrees with each of the individual values to

Table 1. *Final atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$), with e.s.d.'s in parentheses, for TlBrO_4 at 294 and 169 K*

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	T(K)	x	y	z	U_{eq}
Tl	294	0.17548 (7)	$\frac{1}{4}$	0.16665 (10)	350 (2)
	169	0.1750 (1)	$\frac{1}{4}$	0.1666 (1)	159 (3)
Br	294	0.0739 (2)	$\frac{1}{4}$	0.6853 (2)	265 (4)
	169	0.0753 (3)	$\frac{1}{4}$	0.6855 (3)	111 (6)
O(1)	294	0.2158 (16)	$\frac{1}{4}$	0.5612 (20)	585 (55)
	169	0.2214 (25)	$\frac{1}{4}$	0.5598 (27)	301 (71)
O(2)	294	0.9227 (16)	$\frac{1}{4}$	0.5798 (22)	669 (63)
	169	0.9255 (22)	$\frac{1}{4}$	0.5752 (30)	290 (72)
O(3)	294	0.0830 (10)	0.0369 (16)	0.8065 (11)	427 (26)
	169	0.0840 (15)	0.0372 (24)	0.8085 (17)	197 (37)

Table 2. *Bond lengths (Å) and angles (°) for thallous perbromate at 294 and 169 K with e.s.d.'s in parentheses*

Perbromate ion	294 K	169 K
Br—O(1)	1.612 (15)	1.642 (22)
Br—O(2)	1.606 (15)	1.606 (21)
Br—O(3), O(3 ⁱⁱ)	1.598 (10)	1.594 (14)
O(1)—O(2)	2.696 (21)	2.707 (30)
O(1)—O(3), O(3 ⁱⁱ)	2.587 (16)	2.610 (23)
O(2)—O(3), O(3 ⁱⁱ)	2.620 (17)	2.629 (23)
O(3)—O(3 ⁱⁱ)	2.598 (14)	2.574 (20)
O(1)—Br—O(2)	113.8 (8)	112.9 (11)
O(1)—Br—O(3), O(3 ⁱⁱ)	107.4 (4)	107.5 (6)
O(2)—Br—O(3), O(3 ⁱⁱ)	109.7 (4)	110.5 (6)
O(3)—Br—O(3 ⁱⁱ)	108.7 (5)	107.7 (7)

Coordination polyhedron	294 K	169 K	294 K	169 K
Tl—O(2 ⁱⁱⁱ)	2.950 (16)	2.938 (21)	Tl—O(1)	3.041 (15)
Tl—O(3 ^{iv})	2.955 (9)	2.943 (14)	Tl—O(3 ^{viii})	3.161 (9)
Tl—O(3 ^v)	2.955 (9)	2.943 (14)	Tl—O(3 ^{ix})	3.161 (9)
Tl—O(3 ^{vi})	3.020 (9)	3.006 (14)	Tl—O(1 ^{vi})	3.307 (6)
Tl—O(3 ^{vii})	3.020 (9)	3.006 (14)	Tl—O(1 ^v)	3.307 (6)

Code for symmetry-related atoms: (i) $x-1, y, z$; (ii) $x, \frac{1}{2}-y, z$; (iii) $x, y, z-1$; (iv) $-x, -y, 1-z$; (v) $-x, y+\frac{1}{2}, 1-z$; (vi) $\frac{1}{2}-x, y+\frac{1}{2}, z-\frac{1}{2}$; (vii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (viii) $x, y, z-1$; (ix) $x, \frac{1}{2}-y, z-1$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$.

within the experimental uncertainty, the mean O—Br—O angle does not so agree with the individual angle values. Accordingly, the principal departure from regular tetrahedral geometry is angular. At 169 K, the Br—O bond lengths range from 1.594(14) to 1.642(22) Å with a mean value of 1.609(9) Å, while the O—Br—O bond angles range from 107.5(6) to 112.9(11)° with a mean value of 109.4(3)° (Table 2). Again, the principal departure from regular tetrahedral geometry is angular. We note that, contrary to expectation, the mean Br—O bond length is slightly (though not statistically significantly) greater for the lower temperature. This is due primarily to what appears to be a high value for the Br—O(1) distance in the low-temperature structure.

The mean values of the Br—O bond lengths reported here are in good agreement with previously reported

* Lists of structure factors and anisotropic thermal parameters for the 294 K and the 169 K structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51604 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

values: for example, at room temperature, 1.603 (6) vs 1.608 (3) Å for barium perbromate (Gerkin, Reppart & Appelman, 1988), and at 169 K, 1.609 (9) vs 1.603 (3) Å for nickel(II) perbromate hexahydrate (Gallucci, Gerkin & Reppart, 1988).

Concerning the coordination polyhedron about thallium, we have shown in Fig. 1 ten perbromate oxygens coordinated to a given thallium and have listed the Tl—O distances in Table 2. It should be noted both that the geometrical arrangement of the coordinating oxygens is not conveyed well by a simple label and, more importantly, that assessment of the number of coordinating oxygens is not unambiguous. In their discussion of the KBrO_4 structure (which is indeed very similar to the TlBrO_4 structures), Siegel, Tani & Appelman (1969) tabulated coordination distances to eight perbromate oxygens and spoke of eightfold coordination. It appears preferable to us to describe the coordination as tenfold (as has been done above and in Fig. 1) or sixfold. As the coordination polyhedron entries in Table 2 show, the six closest O neighbors of Tl are spread over a range of distance of only ~ 0.1 Å. In order to reach the seventh and eighth O neighbors the range must then be increased ~ 0.1 Å — a distance

as great as the entire range of distances for the first six oxygens. Moreover, lying just another ~ 0.14 Å beyond the seventh and eighth neighbors are the ninth and tenth. Beyond these, however, one must proceed ~ 0.4 Å further to encounter the eleventh and twelfth neighbors. This spatial distribution of O neighbors appears inconsistent with a satisfactory description of the coordination as eightfold. The average Tl—O coordination distance for the tenfold coordination choice is 3.09 Å, while for the sixfold choice it would be 2.99 Å.

The 294 K structure appears overall to be somewhat better determined than the 169 K structure. This difference is consistent with the larger size and the higher 2θ collection limit of the 294 K data set.

By the conclusion of the data collections, the crystals were of light orange hue. As stated earlier, however, no decay was indicated by the X-ray data. These observations are consistent with production of quite small amounts of a species with high optical absorption. Br_2 appears to be an acceptable possibility.

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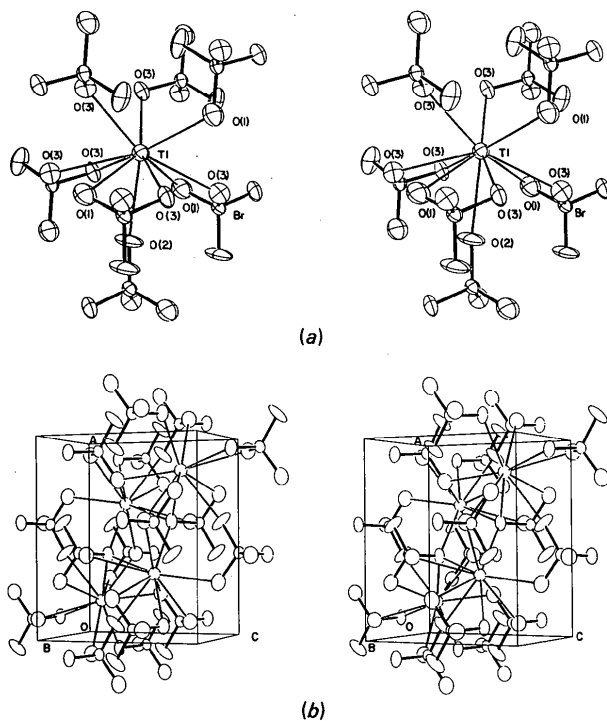


Fig. 1. (a) Stereoview depicting the tenfold coordination of a thallous ion by perbromate oxygen atoms in TlBrO_4 at room temperature. (b) Stereoview of a portion (including a unit cell) of the TlBrO_4 structure at room temperature. Drawn using ORTEPII (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms.