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A second polymorph of 1,1,4,4-tetramethylpiperazinium pentabromothallate(III)

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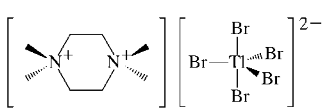
A new polymorph of the title compound, $(C_8H_{20}N_2)[TlBr_5]$, contains cations located about crystallographic centres of inversion and trigonal-bipyramidal anions which have a C_2 axis passing through the equatorial plane of the anion. The anion has the least distorted geometry seen so far in any structure possessing this anion and the axial Tl—Br bonds are about 0.13 Å longer than the equatorial Tl—Br bonds, consistent with related structures. The anion in the initially reported polymorph has lower symmetry and a greater distortion of the trigonal-bipyramidal coordination.

Comment

The pentacoordinate $[TlBr_5]^{2-}$ anion was characterized only recently as an almost regular trigonal-bipyramidal species in its 1,1,4,4-tetramethylpiperazinium, (I), and *N,N'*-diethyltriethylenediammonium salts (Linden, Nugent *et al.*, 1999). In both cases, the Br_{ax}—Tl—Br_{ax} angles (ax is axial) were somewhat distorted from linearity and the Tl—Br_{ax} bond distances were quite asymmetric, but significantly longer than the Tl—Br_{eq} distances (eq is equatorial). Thus, the anion in these two compounds was shown to have a similar structure to that found for $[FeCl_5]^{2-}$ in its complex with a quaternized



(I*b*)

ammonium counter-cation (James *et al.*, 1995), but is different from the distorted square-pyramidal $[InCl_5]^{2-}$ anion found in its tetraethylammonium salt (Joy *et al.*, 1975). During an evaluation of currently available commercial diffractometers having CCD detectors, data sets were collected from a series of crystals with known 'difficult' structures (Linden, 1999). One of the compounds chosen was the title compound, (I). A crystal from the original batch was selected and found to exist as a different form, (I*b*), to that found in the original structure determination (I*a*; Linden, Nugent *et al.*, 1999). It is unknown whether both forms existed simultaneously in the original batch at the time of crystallization, or if this second form evolved from the former structure during the three years that the original crystals were stored.

The original structure determination for the title compound found that the space group was $P2_1/c$ with two symmetry-independent 1,1,4,4-tetramethylpiperazinium cations sitting across centres of inversion and one unique $[TlBr_5]^{2-}$ anion in a general position. In contrast, polymorph (I*b*) crystallizes in space group $C2/c$ with one unique cation possessing crystallographic C_i symmetry and one unique anion with crystallographic C_2 symmetry (Fig. 1). Although the unit-cell volumes of the two polymorphs are quite similar, as are the lengths of the b axes and the β angles, the lengths of the a and c axes show significant differences and no transformation matrix can be found which will interconvert the two unit cells, thus excluding the possibility that the lower symmetry polymorph was simply defined in the wrong space group.

The twofold axis through the $[TlBr_5]^{2-}$ anion of (I*b*) passes through the equatorial plane of the anion, one of the equatorial Br atoms and the Tl atom. As a result, both axial Tl—Br bonds are equal in length and the coordination geometry of the anion forms quite a regular trigonal bipyramid, although the symmetry does not constrain it to be a perfect one. Indeed, the axial Tl—Br bonds are slightly distorted from linear geometry by 2.968 (17)° (Table 1) and are also about 0.13 Å longer than the equatorial Tl—Br bonds.

The structures of just four other compounds containing almost regular trigonal-bipyramidal $[TlBr_5]^{2-}$ anions are reported in the literature (Linden, Nugent *et al.*, 1999; Reid *et al.*, 1999; Linden *et al.*, 2002), although other much more highly distorted $[TlBr_5]^{2-}$ species are known (Linden, James *et al.*, 1999; Linden *et al.*, 2002). Of these four compounds, two possess $[TlBr_5]^{2-}$ anions with crystallographic symmetry, namely C_2 symmetry in the *N,N'*-diethyl-*N,N,N',N'*-tetramethyl-1,2-ethylenediammonium salt (etmeen; Linden *et al.*, 2002) and C_{2v} symmetry in the $[Mn(15\text{-crown-}5)(H_2O)_2]^{2+}$ salt

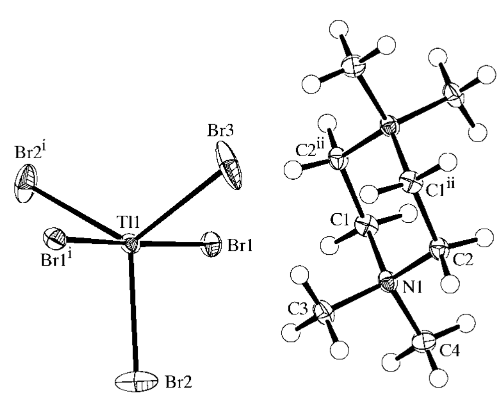


Figure 1
The structure of (I*b*) drawn with 50% probability displacement ellipsoids and showing the atom-numbering scheme. H atoms are represented by circles of arbitrary size. [Symmetry codes: (i) $2 - x, y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.]

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[Mn(crown); Reid *et al.*, 1999]. The geometric parameters for each of these anions are included in Table 1 and show that the anion in (I*b*) has the least distorted trigonal-bipyramidal geometry of the three structures. The Br_{ax}—Tl—Br_{ax} bonds in the anion of the etmeen salt show the greatest deviation from linearity [7.25 (6)°], although these distortions are still quite small. While the Tl—Br bond lengths in this latter salt are very similar to those of (I*b*), the axial Tl—Br bonds in the Mn(crown) salt are significantly longer than in (I*b*) and the equatorial bonds are correspondingly shorter, the difference between the axial and equatorial bond lengths now being about 0.34 Å.

The two reported structures in which the $[TlBr_5]^{2-}$ anions do not possess any crystallographic symmetry are those of the first polymorph of the title compound, (I*a*), and the *N,N'*-diethyltriethylenediammonium salt (Linden, Nugent *et al.*, 1999). The Br_{ax}—Tl—Br_{ax} angles are distorted from linearity by 2.67 (4)° in (I*a*), and by 10.3 (2) and 6.3 (2)° for the two symmetry-independent anions in the latter structure. Thus, the distortions from linearity are similar to those observed in (I*b*) and the other structures in which the anions have crystallographic symmetry. The lengths of the equatorial Tl—Br bonds of these two compounds, being about 2.59 Å, are also similar to those of (I*b*) and are shorter than the axial Tl—Br bonds, as expected. However, in contrast to (I*b*) and the other symmetrical anions, the lengths of the axial Tl—Br bonds in these two compounds show distinct asymmetry. In (I*a*), these distances are 2.840 (1) and 2.737 (1) Å, while for the *N,N'*-diethyltriethylenediammonium salt, they are 2.914 (4) and 2.706 (4) Å, and 2.915 (5) and 2.725 (5) Å for the two symmetry-independent anions, respectively. This asymmetry leads to a significant distortion of the trigonal bipyramid in that the Tl—Br bonds involving the equatorial Br atoms are bent at the Tl atom away from the closer of the two axial Br atoms towards the more distant one, resulting in a deviation of some Br_{ax}—Tl—Br_{eq} angles by up to 10° from the ideal value of 90° and a deviation of the Tl atom from the equatorial plane of Br atoms by between 0.10 and 0.18 Å (Linden, Nugent *et al.*, 1999). Such asymmetry and distortions of the trigonal bipyramid are not observed in the structure of (I*b*) and the Tl atom lies of necessity on the equatorial plane.

The crystal packing consists of alternating layers of cations and anions stacked parallel to the (100) plane.

Experimental

The title compound was prepared as described previously (Linden, Nugent *et al.*, 1999) and crystallized by slow evaporation of its solution in concentrated HBr (m.p. 494–497 K).

Crystal data

$(C_8H_{20}N_2)[TlBr_5]$	D_x = 2.766 Mg m^{-3}
M_r = 748.15	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2872 reflections
a = 16.0822 (3) Å	θ = 2.9–36.4°
b = 9.2422 (2) Å	μ = 20.09 mm^{-1}
c = 13.2718 (2) Å	T = 173 (1) K
β = 114.3928 (8)°	Prism, yellow
V = 1796.56 (6) Å^3	0.26 × 0.23 × 0.21 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	2467 reflections with $I > 2\sigma(I)$
φ scans, and ω scans with κ offsets	R_{int} = 0.080
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	θ_{max} = 30.5°
T_{min} = 0.074, T_{max} = 0.105	$h = 0 \rightarrow 22$
18 998 measured reflections	$k = 0 \rightarrow 13$
2740 independent reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 10.0125P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.068	$\Delta\rho_{max}$ = 2.22 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −2.26 e Å^{-3}
2740 reflections	Extinction correction: *SHELXL*97
77 parameters	Extinction coefficient: 0.00183 (8)
H-atom parameters constrained	

Table 1
Comparison of selected geometric parameters (Å,°) for (I*b*) with those of other $[TlBr_5]^{2-}$ salts containing symmetrical anions.

	(I*b*)	Mn(crown) salt[a,b]	etmeen salt[c]
Tl1—Br1	2.7350 (4)	2.883 (2)	2.762 (2)
Tl1—Br2	2.5915 (5)	2.540 (2)	2.596 (2)
Tl1—Br3	2.6237 (7)	2.552 (3)	2.619 (2)
Br1—Tl1—Br1^{i}	177.032 (17)	175.36 (9)	172.75 (6)
Br1—Tl1—Br2	90.585 (14)	88.97	91.61 (5)
Br1—Tl1—Br2^{i}	90.910 (14)	88.97	92.56 (5)
Br1—Tl1—Br3	88.516 (9)	92.32	86.37 (3)
Br2—Tl1—Br2^{i}	119.46 (3)	127.15 (10)	109.89 (8)
Br2—Tl1—Br3	120.270 (14)	116.43 (5)	125.05 (4)

Symmetry code [applies to (I*b*) only]: (i) $2-x, y, \frac{3}{2}-z$. Notes: (*a*) Reid *et al.* (1999); (*b*) original atom numbering altered to match that of (I*b*); (*c*) Linden *et al.* (2002).

The absorption correction was based on a comparison of the intensities of equivalent reflections in the highly redundant data, as described by Blessing (1995). Attempts at applying a numerical absorption correction yielded significantly inferior results, presumably because the multi-faceted nature of the crystal inhibited the development of an accurate description of the crystal shape. The largest seven peaks of residual electron density (from 2.22 down to 1.00 e Å^{-3}) were all within 1.2 Å of the Tl or Br atoms. The methyl H atoms were constrained to an ideal geometry, with C—H distances of 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—N bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *KappaCCD Server Software* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1524). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

James, B. D., Liesegang, J., Bakalova, M., Reiff, W. M., Skelton, B. W. & White, A. H. (1995). *Inorg. Chem.* **34**, 2054–2057.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Joy, G., Gaughan, A. P., Wharf, I., Shriver, D. F. & Dougherty, J. P. (1975). *Inorg. Chem.* **14**, 1795–1801.

Linden, A. (1999). XVIIIth IUCr Congress and General Assembly, Glasgow, Scotland. Abstract M08.OE.005.

Linden, A., James, M. A., Milliken, M. B., Kivlighon, L. M., Petridis, A. & James, B. D. (1999). *Inorg. Chim. Acta*, **284**, 215–222.

Linden, A., Nugent, K. W., Petridis, A. & James, B. D. (1999). *Inorg. Chim. Acta*, **285**, 122–128.

Linden, A., Petridis, A. & James, B. D. (2002). *Inorg. Chim. Acta.* In the press.

Nonius (1999). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.

Reid, H. O. N., Kahwa, I. A., White, A. J. P. & Williams, D. J. (1999). *J. Chem. Soc. Chem. Commun.* pp. 1565–1566.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.