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Intermolecular interactions in 2,5-dimethylpyrazinium tetrabromidothallate(III)

Rawhi Al-Far[a] and Basem Fares Ali[b]*

[a]Faculty of Science and IT, Al-Balqa'a Applied University, Salt, Jordan, and [b]Department of Chemistry, Al al-Bayt University, Mafraq 25113, Jordan
Correspondence e-mail: bfali@aabu.edu.jo

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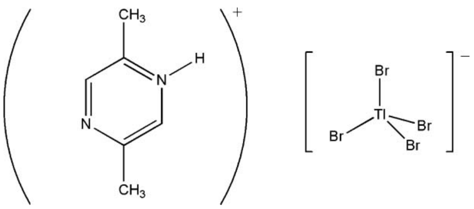
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.016 Å; disorder in main residue; R factor = 0.026; wR factor = 0.049; data-to-parameter ratio = 20.1.

In the title compound, $(C_6H_{10}N_2)[TlBr_4]$, the asymmetric unit contains one half-cation and one half-anion, where the Tl atom has a distorted tetrahedral environment. The Tl atom and two Br atoms lie on a mirror plane; the cation is centrosymmetric, with the H atom disordered over both N atoms. In the crystal structure, the cations and anions are packed into alternate stacks, with no significant intermolecular Br···Br and/or aryl–aryl interactions within each stack. The anion–anion stacks interact *via* Br···Br interactions [Br···Br = 3.6368 (16) Å] to form one-dimensional arrays. The Br···aryl interactions are arranged in a ···aryl···Br···ar-Br···aryl···Br··· infinite motif [Br···centroid distance 4.07 (1) Å], linking the anions and cations into two-dimensional layers.

Related literature

For general background, see: Abdi *et al.* (2004); Castiñeiras *et al.* (1991); Cui *et al.* (2000); Lacroix *et al.* (1994); Chakravarthy & Guloy (1997); Huang & Wang (2007); Al-Far & Ali (2007*b*). For related literature, see: Abdi *et al.* (2005); He *et al.* (2002); Linden *et al.* (2002); Al-Far & Ali (2007*a*); Hao & Liu (2007); Churakov *et al.* (2006); Yang *et al.* (2004).



Experimental

Crystal data

$(C_6H_{10}N_2)[TlBr_4]$
$M_r = 634.14$
Monoclinic, $P2_1/m$
$a = 6.747$ (2) Å
$b = 14.6689$ (7) Å
$c = 6.9651$ (7) Å
$\beta = 90.01$ (1)°
$V = 689.3$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 23.27$ mm^{-1}
$T = 298$ (2) K
0.15 × 0.10 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.074$, $T_{max} = 0.192$
4843 measured reflections
1304 independent reflections
1290 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.049$
$S = 0.86$
1304 reflections
65 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Tl1—Br1	2.5473 (13)	Tl1—Br3	2.5519 (8)
Tl1—Br2	2.544 (3)		
Br2—Tl1—Br1	111.48 (5)	Br1—Tl1—Br3	108.88 (3)
Br2—Tl1—Br3	107.71 (3)	Br3—Tl1—Br3^{i}	112.19 (5)

Symmetry code: (i) $x, -y+\frac{1}{2}, z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2276).

References

Abdi, M., Zouari, F. & Ben Salah, A. (2004). *J. Chem. Crystallogr.* **34**, 673–677.
Abdi, M., Zouari, F., Chniba-Boudjada, N., Bordet, P. & Salah, A. B. (2005). *Acta Cryst.* E**61**, m240–m241.
Al-Far, R. & Ali, B. F. (2007*a*). *Acta Cryst.* E**63**, m1701.
Al-Far, R. & Ali, B. F. (2007*b*). *J. Chem. Crystallogr.* **37**, 333–341.
Bruker (2001). *SMART*. Version 5.630. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *SHELXTL* (Version 6.14) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2006). *SAINT*. Version 7.23a. Bruker AXS Inc., Madison, Wisconsin, USA.
Castiñeiras, A., Bermejo, M. R., Garcia-Deibe, A. & Hiller, W. (1991). *Acta Cryst.* C**47**, 1738–1740.
Chakravarthy, V. & Guloy, A. M. (1997). *Chem. Commun.* pp. 697–698.
Churakov, A. V., Kuz'mina, L. G., Prikhodchenko, P. V. & Howard, J. A. K. (2006). *Acta Cryst.* E**62**, o2265–o2267.

doi:10.1107/S1600536807036513

Cui, Y., Ren, J., Chen, G., Yu, W.-C. & Qian, Y. (2000). *Acta Cryst.* C**56**, e552–e553.

Hao, L.-J. & Liu, T.-T. (2007). *Acta Cryst.* E**63**, m169–m171.

He, Z., Zhu, M. & Ma, G. (2002). *Acta Cryst.* E**58**, m647–m649.

Huang, P.-Y. & Wang, J.-G. (2007). *Acta Cryst.* E**63**, m645–m646.

Lacroix, P. G., Clement, R., Nakatani, K., Zyss, J. & Ledoux, I. (1994). *Science*, **263**, 658–660.

Linden, A., Petridis, A. & James, B. D. (2002). *Acta Cryst.* C**58**, m53–m55.

Yang, M., Ni, C., Zheng, Y. & Gu, W. (2004). *Acta Cryst.* E**60**, m833–m835.

supplementary materials

Acta Cryst. (2007). E**63**, m2242-m2243 [**doi:10.1107/S1600536807036513**]

Intermolecular interactions in 2,5-dimethylpyrazinium tetrabromidothallate(III)

R. Al-Far and **B. F. Ali**

Comment

A large number of Tl(III)-organic complexes are known and their main crystallographic details have also been surveyed and reported (Abdi *et al.*, 2004 and references therein). However, Tl(III) complexes containing Tl(III) anionic species-organic cations are relatively small (Abdi *et al.*, 2004; Castineiras *et al.*, 1991). On the other hand, the research in the field of inorganic-organic hybrids is of great interest due to their magnetic, electronic and optoelectric properties (Cui *et al.*, 2000; Chakravarthy & Guloy, 1997; Lacroix *et al.*, 1994). The packing interactions that govern the crystal organization is expected to affect the packing and then the specific properties of such solids. For example, pyrazine (pyz) and similar ligands have been used through their two nitrogen atoms as neutral linkers to generate and stabilize many open 1-, 2- and 3-D coordination polymers and forming supramolecular coordination assemblies (Hao & Liu, 2007; Huang & Wang, 2007). We herein report the crystal structure of the title complex, (I), wherein, the protonated dimethylpyrazinium ligand $[pyzH]^+$ is not involved in coordination, but in extensive infinite aryl···Br···aryl···Br intermolecular interactions, affording a 2-D network structure by the aid of Br···Br interactions.

The asymmetric unit of the title compound, (I), contains one half $[pyzH]^+$ cation and $[TlBr_3]^-$ unit of the anion, where the Tl atom has a distorted tetrahedral environment (Fig. 1, Table 1). The Tl—Br bonds and Br—Tl—Br angles are in the range of 2.5452 (13)–2.5518 (9) Å [mean value is 2.5481 (12) Å] and 107.70 (4)–112.20 (5)°, respectively, in which they are in accordance with the corresponding values (Abdi *et al.*, 2005; He *et al.*, 2002; Linden *et al.*, 2002). On the other hand, in the cation the bond lengths and angles are the same as those reported (Al-Far & Ali, 2007*a*; Hao & Liu, 2007; Churakov *et al.*, 2006; Yang *et al.*, 2004).

The molecules of discrete anions, packed into stacks, are separated by stacks of cations. The anion stacks along the *c* axis are parallel to the cation stacks with Tl···Tl distance of 6.9651 (7) Å, with no significant interactions between anions and cations within a stack. Inter anion-stacks are linked only through one Br···Br interaction parallel to *b* axis [$Br3\cdots Br3^{ii}$ = 3.6368 (16) Å (symmetry code (ii): $-x, -y, -z$)]. The anions and cations are not involved in any of Br···H interactions, but only through Br···aryl interactions, that are represented in the ···aryl···Br···aryl···Br··· infinite motif (Al-Far & Ali, 2007*a*,b), in which the bromide ions of the anion lie between the two cationic species with centroid···Br···centroid (symmetry code: x, y, z) repeat distance of 4.07 (1) Å. Beside these interactions along with inter anion-stacks, the Br···Br interactions link the anions and cations together into 2-D layers approximately normal to the *a* axis (Fig 2).

Experimental

For the preparation of (I), $TlBr_3\cdot 4H_2O$ (258 mg, 0.5 mmol) dissolved in absolute ethanol (10 ml) and liquid Br_2 (20%, 2 ml), was added dropwise to a stirred hot ethanolic solution of 2,5-dimethylpyrazine (75%, 1 ml) dissolved in ethanol (10 ml) and HBr (60%, 2 ml). After heating for 2 h, the mixture was filtered off and allowed to stand undisturbed at room temperature. The salt crystallized out over 3 d as yellow blocks. Crystals were filtered off, washed with ethanol then diethylether, and dried under vacuum (yield; 200 mg, 62.9%).

Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å (for NH) and C—H = 0.93 and 0.96 Å for aromatic and methyl H atoms, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C,N)$, where $x = 1.5$ for methyl H, and $x = 1.2$ for all other H atoms.

Figures

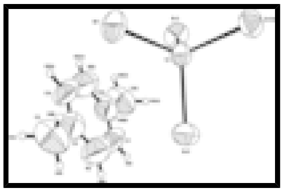

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code A: *x*, 1/2 − *y*, *z*].

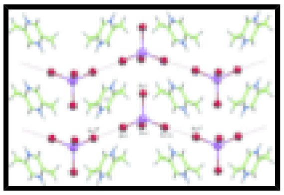

Fig. 2. A partial packing diagram for (I), viewed down the *c* axis (a is vertical and b is horizontal). The Br···aryl interaction is shown as Br2 and X1 [centroid of cation generated by *x*, *y*, *z*] and Br···Br interactions are shown as dashed lines [symmetry codes: (A) *x*, 1/2 − *y*, *z*, (i) −*x*, 1/2 + *y*, −*z*, (ii) −*x*, −*y*,-*z*].

2,5-dimethylpyrazinium tetrabromidothallate(III)

Crystal data

$(C_6H_{10}N_2)[TlBr_4]$	$F_{000} = 562$
$M_r = 634.14$	$D_x = 3.055$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2yb	Cell parameters from 1290 reflections
a = 6.747 (2) Å	θ = 1.8–25.3°
b = 14.6689 (7) Å	μ = 23.27 mm^{-1}
c = 6.9651 (7) Å	*T* = 298 (2) K
β = 90.01 (1)°	Block, yellow
V = 689.3 (2) Å^3	0.15 × 0.10 × 0.07 mm
Z = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	1304 independent reflections
Radiation source: fine-focus sealed tube	1290 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.045$
Detector resolution: 8.3 pixels mm^{-1}	$\theta_{max} = 25.2°$
T = 298(2) K	$\theta_{min} = 2.9°$
ω scans	*h* = −8→8
Absorption correction: multi-scan	*k* = −17→17

(SADABS; Bruker, 2004)	
$T_{\min} = 0.074$, $T_{\max} = 0.192$	$l = -8\rightarrow 8$
4843 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.026$	H-atom parameters constrained
$wR(F^2) = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0135P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.86$	$(\Delta/\sigma)_{\max} < 0.001$
1304 reflections	$\Delta\rho_{\max} = 0.48$ e Å^{-3}
65 parameters	$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Tl1	0.19905 (6)	0.2500	0.28087 (6)	0.05200 (14)
Br1	0.0840 (2)	0.2500	0.62919 (18)	0.0897 (4)
Br2	0.57533 (16)	0.2500	0.2570 (2)	0.0760 (4)
Br3	0.07269 (13)	0.10561 (5)	0.11722 (13)	0.0700 (2)
C1	0.6282 (15)	−0.0176 (8)	0.3530 (18)	0.096 (3)
H1A	0.7202	−0.0285	0.2562	0.115*
N2	0.6727 (13)	0.0396 (8)	0.5027 (19)	0.125 (4)
H2A	0.7861	0.0663	0.5041	0.150*
C3	0.5420 (17)	0.0558 (7)	0.6508 (17)	0.093 (3)
C4	0.5876 (19)	0.1147 (8)	0.8054 (18)	0.120 (4)
H4A	0.5889	0.0805	0.9230	0.180*
H4B	0.4892	0.1618	0.8133	0.180*
H4C	0.7155	0.1416	0.7848	0.180*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tl1	0.0567 (2)	0.0512 (2)	0.0481 (2)	0.000	0.00006 (17)	0.000
Br1	0.0977 (9)	0.1257 (11)	0.0456 (7)	0.000	0.0098 (7)	0.000
Br2	0.0536 (6)	0.0877 (8)	0.0869 (9)	0.000	−0.0051 (6)	0.000
Br3	0.0787 (5)	0.0604 (5)	0.0710 (6)	−0.0134 (3)	0.0036 (5)	−0.0109 (4)
C1	0.087 (7)	0.100 (7)	0.101 (9)	0.019 (6)	0.047 (7)	0.017 (7)
N2	0.091 (6)	0.120 (8)	0.164 (11)	0.016 (5)	0.027 (8)	0.047 (8)
C3	0.091 (7)	0.097 (7)	0.093 (8)	0.039 (6)	0.017 (7)	0.021 (6)
C4	0.126 (9)	0.120 (9)	0.114 (10)	0.039 (7)	−0.020 (9)	−0.028 (8)

Geometric parameters (Å, °)

Tl1—Br1	2.5473 (13)	N2—C3	1.378 (12)
Tl1—Br2	2.544 (3)	N2—H2A	0.8600
Tl1—Br3	2.5519 (8)	C3—C1$^{\mathrm{ii}}$	1.278 (14)
Tl1—Br3$^{\mathrm{i}}$	2.5519 (8)	C3—C4	1.414 (15)
C1—C3$^{\mathrm{ii}}$	1.278 (14)	C4—H4A	0.9600
C1—H1A	0.9300	C4—H4B	0.9600
N2—C1	1.372 (14)	C4—H4C	0.9600
Br2—Tl1—Br1	111.48 (5)	C3—N2—H2A	118.8
Br2—Tl1—Br3	107.71 (3)	C1$^{\mathrm{ii}}$—C3—N2	118.9 (12)
Br1—Tl1—Br3	108.88 (3)	C1$^{\mathrm{ii}}$—C3—C4	118.6 (12)
Br2—Tl1—Br3$^{\mathrm{i}}$	107.71 (3)	N2—C3—C4	122.4 (12)
Br1—Tl1—Br3$^{\mathrm{i}}$	108.88 (3)	C3—C4—H4A	109.5
Br3—Tl1—Br3$^{\mathrm{i}}$	112.19 (5)	C3—C4—H4B	109.5
C3$^{\mathrm{ii}}$—C1—N2	118.7 (11)	H4A—C4—H4B	109.5
C3$^{\mathrm{ii}}$—C1—H1A	120.6	C3—C4—H4C	109.5
N2—C1—H1A	120.6	H4A—C4—H4C	109.5
C1—N2—C3	122.3 (10)	H4B—C4—H4C	109.5
C1—N2—H2A	118.8		
C3—N2—C1—C3$^{\mathrm{ii}}$	1.4 (18)	C1—N2—C3—C4	179.9 (10)
C1—N2—C3—C1$^{\mathrm{ii}}$	−1.4 (18)		

Symmetry codes: (i) *x*, −*y*+1/2, *z*; (ii) −*x*+1, −*y*, −*z*+1.

Fig. 1

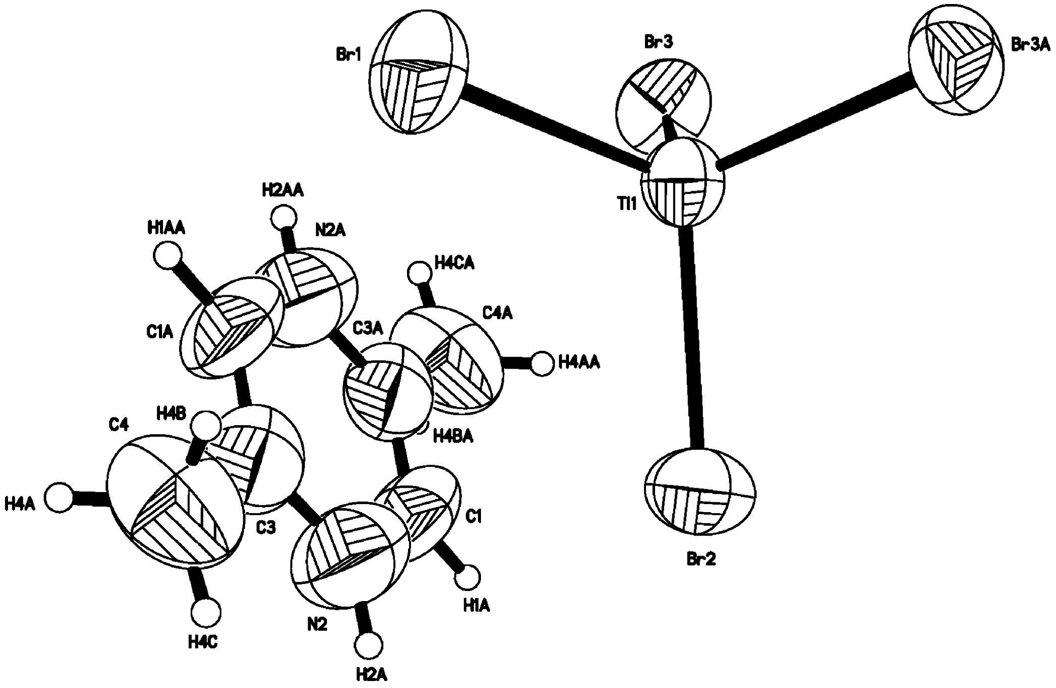
Br1
Br3
Br3A
Tl1
Br2
H2AA
H1AA
N2A
H4CA
C4A
C1A
C3A
H4AA
H4B
C4
H4BA
H4A
C3
C1
H1A
H4C
N2
H2A

Fig. 2