1,1-Dimethylbiguanidium tetrabromothallate(III)

Zhenliang He,ª Miaoli Zhu[b]**† and Guibin Ma**[a]*****

ªSchool of Chemistry and Chemical Engineering, University of Shanxi, Taiyuan, Shanxi 030006, People's Republic of China, and [b]Institute of Molecular Science, University of Shanxi, Taiyuan, Shanxi 030006, People's Republic of China

† Additional correspondence author, email: miaoli@sxu.edu.cn.

Correspondence e-mail: maguibin@sxu.edu.cn

The title compound, $(C_4H_{12}N_5)[TlBr_4]$, was crystallized from an aqueous solution containing $[Tl(DMSO)_6](ClO_4)_3$, N,N-dimethylbiguanide hydrochloride and NaBr in a 1:1:3 molar ratio (DMSO is dimethyl sulfoxide). The geometry of $[TlBr_4]^-$ is a slightly distorted tetrahedron. The cation is protonated at one of the imino groups, and through this an intramolecular N—H···N hydrogen bond is formed, which stabilizes the conformation of the cation in the structure.

Comment

The formation and equilibrium of Tl^{III}–halide complexes has been extensively studied in solution by NMR techniques (Glaser, 1995). In the solid state, various compounds with composition $[TlX_n]^{(n-3)-}$ ($n = 4$, 5 and 6 for Cl^- and Br^-; $n = 4$ for I^-) have been characterized (Lee, 1971). A few crystal structures of Tl^{III}–halide complexes have been studied by X-ray analysis (Glaser, 1995; Ma *et al.*, 2002). The coordination geometry of Tl^{III} is quite versatile, with different kinds of ligands, and the coordination number can range from four to eight (Kritikos *et al.*, 2002). Recently, it has been found that various organic cations can stabilize the pentabromothallate(III) anion in the solid state (Linden, James *et al.*, 1999; Linden, Nugent *et al.*, 1999; Linden *et al.*, 2002). The structural versatility of Tl^{III}–halide complexes has prompted us to synthesize and study structures of Tl^{III} halides complexes with different organic molecules.

(I)
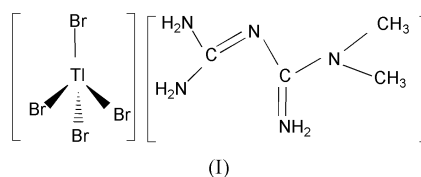
Dimethylbiguanide (MET) is an oral hypoglycaemic drug and is found to have fewer side effects than other biguanides, *e.g.* phenformin (Herrnstadt *et al.*, 1979). The crystal structure of its hydrochloride (N,N-dimethylbiguanide hydrochloride, $C_4H_{11}N_5 \cdot HCl$) has been determined, and the molecular conformation is stabilized by five symmetry-independent N—H···N and N—H···Cl hydrogen bonds (Hariharan *et al.*, 1989). The deprotonated molecule can be used as a monodentate or bidentate ligand to form complexes with Zn^{II}, Cu^{II} and Ni^{II} (Zhu *et al.*, 2002; Zhu *et al.*, 2002a,b). In an attempt to prepare the mixed-ligand thallium(III) complex $[TlBr_3(C_4H_{11}N_5)]$, the title complex, (I), was obtained. In this product, MET, instead of acting as a monodentate or bidentate ligand to form the desired complex, is protonated as a cation to stabilize the $TlBr_4^-$ anion, forming a salt.
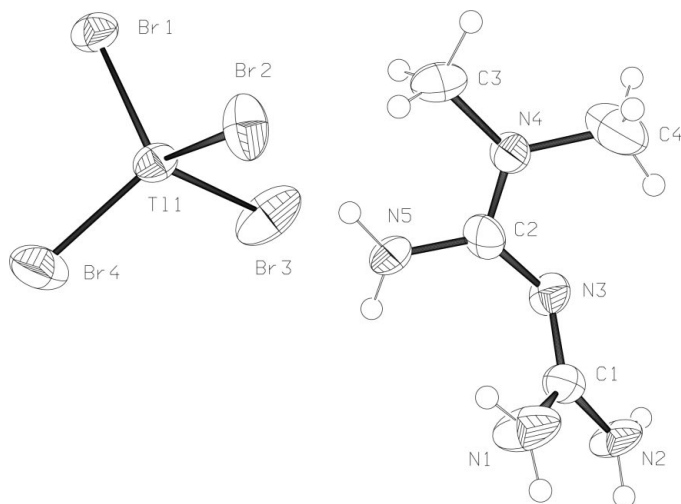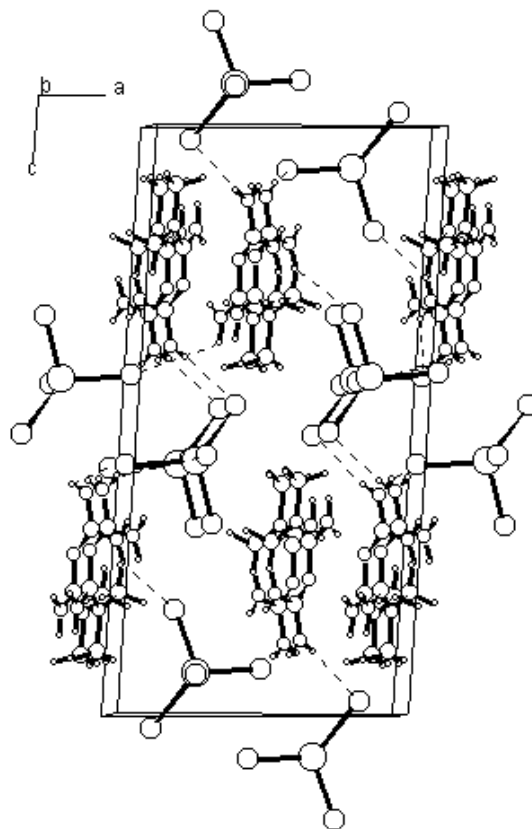
Figure 1
A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii.

A number of crystal structures of the $[TlBr_4]^-$ anion with different cations (Tl^+, K^+, NH_4^+, Rb^+, and Cs^+) have been reported in the literature (Glaser, 1980). Selected geometric parameters for (I) are listed in Table 1, and a perspective view of the structure is shown in Fig. 1. Except for a slight distortion from ideal tetrahedral geometry, probably due to packing effects, the geometry of $[TlBr_4]^-$ here is similar to previously reported results (Glaser, 1980). In the cation, the site of protonation is the same as in 1,1-dimethylbiguanide hydrochloride, but the cation conformation in (I) is slightly different. There are N—H···Br intermolecular hydrogen bonds between the cations and anions. Hydrogen-bond parameters are listed in Table 2, and a packing diagram is shown in Fig. 2. A weak N1—H···N5 intramolecular hydrogen bond stabilizes the cation conformation (Fig. 1). It should be noted that the H-atom positions were calculated and not refined, in the presence of the heavy atoms Tl and Br.

It is interesting to compare the bond lengths in the free molecule and in the coordinated ligand. The C—C and C—N bond distances of the cation are shorter than typical single bonds and longer than double bonds, showing that the bonding is conjugated. In the structures of Ni^{II} and Cu^{II} complexes of MET, the bond lengths C2—N5 and C1—N1 do not change much relative to the free ligand, while C1—N2, C2—N3 and C1—N3 are longer by about 0.1 Å for C1—N2, and 0.02 Å for C2—N3 and C1—N3; N1 and N5 are the coordinating atoms, and the conformation of the ligand changes on coordination (Zhu *et al.*, 2002*a*,*b*). In $[ZnCl_3(C_4H_{12}N_5)]$ (Zhu *et al.*, 2002), MET coordinates as a monodentate ligand through N3, and the bond lengths C1—N3 and C2—N3 become longer (by 0.03 and 0.05 Å, respectively) than in the free ligand; other bond lengths become only slightly longer. The change in conformation of MET is smaller in the Zn complex than for the Cu and Ni complexes.

Calculation of the species distribution for the Tl—Br system at the molar ratio $Br^-/Tl^{3+} = 3$ in aqueous solution gives molar

Figure 2
A packing diagram, viewed along the *b* axis. The dotted lines represent hydrogen bonds.

fractions for $TlBr_2^+$, $TlBr_3$ and $TlBr_4^-$ of roughly 0.15, 0.70 and 0.15, respectively. Thus, the $C_4H_{12}N_5^+$ cation stabilizes the $[TlBr_4]^-$ anion, to generate the title salt as a solid.

Experimental

Commercial AR-grade 1,1-dimethylbiguanide hydrochloride and NaBr were used without further purification. The title compound was synthesized by preparing a 1:1:3 molar ratio of $[Tl(DMSO)_6](ClO_4)_3$ (Ma *et al.*, 2001), 1,1-dimethylbiguanide (MET) and NaBr in aqueous solution. Colourless crystals were obtained from the solution after one week, by slow evaporation of water.

Crystal data

$C_4H_{12}N_5^+ \cdot TlBr_4^-$	$D_x = 2.991$ Mg m^{-3}
$M_r = 654.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1370
$a = 10.191$ (2) Å	reflections
$b = 6.9540$ (14) Å	$\theta = 2.3$–21.1°
$c = 20.544$ (4) Å	$\mu = 22.10$ mm^{-1}
$\beta = 93.77$ (3)°	$T = 293$ (2) K
$V = 1452.8$ (5) Å^3	Block, colourless
$Z = 4$	$0.23 \times 0.11 \times 0.11$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2478 independent reflections
	1494 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.073$
Absorption correction: multi-scan	$\theta_{max} = 24.8°$
(*SADABS*; Sheldrick, 1996)	$h = -12 \rightarrow 11$
$T_{min} = 0.036$, $T_{max} = 0.088$	$k = -8 \rightarrow 7$
6686 measured reflections	$l = -24 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2478 reflections	$\Delta\rho_{max} = 1.97$ e Å^{-3}
129 parameters	$\Delta\rho_{min} = -1.70$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Tl1—Br3	2.457 (2)	C1—N3	1.329 (15)
Tl1—Br4	2.5207 (19)	C2—N4	1.291 (16)
Tl1—Br2	2.5570 (18)	C2—N3	1.329 (15)
Tl1—Br1	2.6827 (17)	C2—N5	1.351 (15)
C1—N2	1.272 (15)	C3—N4	1.436 (15)
C1—N1	1.311 (16)	C4—N4	1.508 (17)
Br3—Tl1—Br4	111.55 (8)	N1—C1—N3	125.1 (13)
Br3—Tl1—Br2	94.56 (8)	N4—C2—N3	118.6 (12)
Br4—Tl1—Br2	118.58 (6)	N4—C2—N5	117.0 (13)
Br3—Tl1—Br1	111.02 (7)	N3—C2—N5	124.2 (13)
Br4—Tl1—Br1	107.64 (6)	C2—N3—C1	124.9 (11)
Br2—Tl1—Br1	112.97 (6)	C2—N4—C3	120.6 (11)
N2—C1—N1	111.1 (12)	C2—N4—C4	120.0 (12)
N2—C1—N3	123.8 (13)	C3—N4—C4	118.8 (11)
N4—C2—N3—C1	127.9 (14)	N2—C1—N3—C2	169.6 (14)
N5—C2—N3—C1	−58 (2)	N1—C1—N3—C2	−12 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$B\cdots$N5	0.86	2.77	3.188 (16)	112
N5—H5$B\cdots$N3^i	0.86	2.23	3.042 (15)	158
N5—H5$A\cdots$Br1^{ii}	0.86	2.79	3.520 (11)	143
N2—H2$B\cdots$Br1^{iii}	0.86	2.59	3.390 (11)	155
N2—H2$A\cdots$Br2^i	0.86	2.97	3.723 (10)	148
N1—H1$B\cdots$Br3^{iv}	0.86	2.67	3.312 (12)	132
N1—H1$A\cdots$Br2^i	0.86	2.75	3.538 (11)	153

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

H atoms attached to C and N atoms were placed in calculated positions (C—H = 0.96 Å and N—H = 0.86 Å) and refined with a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq} of their respective parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1994–1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

References

Bruker (1994–1996). *SAINT*. Version 4.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1998). *SMART*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Glaser, J. (1980). *Acta Chem. Scand. Ser.* A, **34**, 157–162.
Glaser, J. (1995). *Advances in Inorganic Chemistry*. Vol. 43, edited by A. G. Sykes, pp. 1–78. New York: Academic Press.
Hariharan, M., Rajan, S. S. & Srinivasan, R.. (1989). *Acta Cryst.* C**45**, 911–913.
Herrnstadt, C., Mootz, D., Wunderlich, H. & Mohrle, H. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 735–740.
Kritikos, M., Ma, G.-B., Bodor, A. & Glaser, J. (2002). *Inorg. Chim. Acta*, **331**, 224–231.
Lee, A. G. (1971). *The Chemistry of Thallium*, pp. 44–88. Amsterdam: Elsevier.
Linden, A., James, M. A., Millikan, 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*, **332**, 61–71.
Ma, G.-B., Molla-Abbassi, A., Kritikos, M., Ilyukhin, A., Kessler, V., Skripkin, M., Sandström, M., Glaser, J., Näslund, J. & Persson, I. (2001). *Inorg. Chem.* **40**, 6432–6438.
Ma, G.-B., Fischer, A, & Glaser, J. (2002). *Acta Cryst.* C**58**, m177–m178.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Zhu, M.-L., Lu, L.-P., Jin, X.-L. & Yang, P. (2002). *Acta Cryst.* C**58**, m158–m159.
Zhu, M.-L., Lu, L.-P., Yang, P. & Jin, X.-L. (2002a). *Acta Cryst.* E**58**, m217–m219.
Zhu, M.-L., Lu, L.-P., Yang, P. & Jin, X.-L. (2002b). *Acta Cryst.* E**58**, m272–m274.