al., 1993). Space group $P2_1/n$ was clearly assigned from the absences of the $0k0$ and $h0l$ reflections. Unfortunately, the integrated intensities from the automatic decomposition method of LeBail (GSAS) were not good enough to solve this structure because of highly overlapped peaks in the presence of α_1 and α_2 lines. Therefore, manual decomposition from *CSD* was used. First, the 2θ range from 7 to 50° was taken where position, shape and intensity were refined for each reflection. Then, the obtained accurate unit-cell dimensions and linear extrapolated peak-shape parameters were used to evaluate integral intensities up to $2\theta = 70°$. Integrated intensities of 286 peaks of the 425 possible reflections were used in direct methods to solve the structure. The intensities of $00l$ reflections were arbitrarily corrected by a factor of 0.67 to reduce the effect of preferred orientation. First, three V and five O atoms were located from the *E* map and then the two O and tetramethylammonium atoms were found from difference Fourier maps. Final full-profile refinement (Fig. 3) was carried out to R(Bragg) = 0.052. The correction given by *CSD* approximation of the preferred orientation $I_{\rm corr}(hkl) = I_{\rm obs}(hkl)[1 + (\tau^2 - 1)\sin^2\varphi]^{-1/2}$ (Pecharskii, Akselrud & Zavalij, 1987) was applied. The resultant preferred orientation correction coefficient was in the range 0.4 for $h00$ reflections to 1.0 for $0kl$ reflections.

Data collection: *DMS Software* (Scintag Inc., 1994). Cell refinement: *CSD*. Data reduction: *CSD*. Program(s) used to solve structure: *CSD*. Program(s) used to refine structure: *CSD*. Molecular graphics: *POLIEDRI* (Pilati, 1990) and *INSIGHT*II (Biosym Technologies, 1995).

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References

Akselrud, L. G., Zavalij, P. Y., Grin, Yu. N., Pecharsky, V. K., Baumgartner, B. & Wolfel, E. (1993). *Mater. Sci. Forum*, **133–136**, 335–340.
Biosym Technologies (1995). *INSIGHT*II. Release 95.0. Biosym Technologies, San Diego, California, USA.
Chirayil, T. A., Zavalij, P. Y. & Whittingham, M. S. (1996*a*). *Solid State Ion.* **84**, 163–168.
Chirayil, T. A., Zavalij, P. Y. & Whittingham, M. S. (1996*b*). *J. Electrochem. Soc.* **143**, L193–L195.
Nazar, L. F., Koene, B. E. & Britten, J. F. (1996). *Chem. Mater.* **8**, 327–329.
Pecharskii, V. K., Akselrud, L. G. & Zavalij, P. Y. (1987). *Sov. Phys. Crystallogr.* **32**, 514–516.
Pilati, T. (1990). *Acta Cryst.* **A46**, C-69.
Scintag Inc. (1994). *DMS Software*. Version 2.91. Scintag Inc., Sunnyvale, CA, USA.
Whittingham, M. S., Guo, J.-D., Chen, R., Chirayil, T., Janauer, G. & Zavalij, P. Y. (1995). *Solid State Ion.* **75**, 257–268.
Zavalij, P. Y., Chirayil, T., Whittingham, M. S., Pecharsky, V. K. & Jacobson, R. A. (1997). *Acta Cryst.* **C53**, 170–171.
Zavalij, P. Y. & Whittingham, M. S. (1996). *Acta Cryst.* **A52**, C-411.
Zavalij, P. Y., Whittingham, M. S., Boylan, E. A., Pecharsky, V. K. & Jacobson, R. A. (1996). *Z. Kristallogr.* **211**, 464.
Zhang, Y., DeBord, J. R. D., O'Connor, C. J., Haushalter, R. C., Clearfield, A. & Zubieta, J. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 989–991.

Acta Cryst. (1997). **C53**, 881–883

Bis(η^6-toluene)thallium(I) 7,8,9,10,11,12-Hexabromo-*closo*-1-carbadodecaborate: a Halocarborane-Bridged Dimer with Heavy Metal–Arene Interactions

Rajeev S. Mathur, Tatiana Drovetskaya and Christopher A. Reed*

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0744, USA. E-mail: careed@chem1.usc.edu

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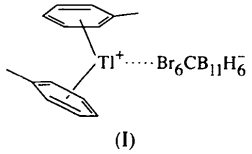
Abstract

The title compound, $[\mathrm{Tl(C_7H_8)_2}](\mathrm{CB_{11}H_6Br_6})$, shows $\mathrm{Tl^+}$ having η^6 interactions with two toluene molecules and dative interactions with two Br atoms of one carborane anion and one Br atom of a neighboring anion.

Comment

The icosahedral carborane anions are an important new class of weakly coordinating anions finding increasing utility in the synthesis of electron-deficient species. The most useful of these are the hexahalogenated derivatives $\mathrm{CB_{11}H_6}X_6^-$ (X = Cl, Br, I), perhaps the most chemically inert and least coordinating anions known to date. They have recently been used to synthesize a salt exhibiting the closest approach to the silylium ion, $R_3\mathrm{Si}^+$ (Reed, Xie, Bau & Benesi, 1993; Xie *et al.*, 1996), an isolable salt of the discrete hydronium ion, $\mathrm{H_9O_4^+}$ (Xie, Bau & Reed, 1995), and the first isolable all-carbon carbocation, the fullerene cation $\mathrm{C_{76}^+}$ (Bolskar, Mathur & Reed, 1996).

A frequently used reaction in this synthetic chemistry is halide abstraction *via* silver salt metathesis. In a number of cases, however, the reaction of a labile metal halide with the silver salt of a weakly coordinating anion does not proceed or is incomplete because of Lewis acid/base adduct formation (Liston, Lee, Scheidt & Reed, 1989). We are therefore investigating the corresponding thallium chemistry and have prepared the thallium(I) salt of the hexabromocarborane $\mathrm{CB_{11}H_6Br_6^-}$ as a new potentially superior halide metathesis reagent, (I). It crystallizes from toluene as a bis(toluene) complex.



(I)

The coordination sphere around Tl^+ is shown in Fig. 1. It comprises two η^6-toluene molecules and three Br-atom donors. Two additional Br atom approaches, Br11 and Br11^i at 4.072 (2) and 4.090 (2) Å, respectively, could be considered weakly interacting [symmetry code: (i) $-x, -y, -z$]. The Tl—Br7, Tl—Br12 and Tl—Br7^i distances are 3.421 (2), 3.393 (2) and 3.592 (2) Å, respectively. These are similar to distances reported in $[(mes)_6Tl_4][GaBr_4]_4$, where mes is 1,3,5-$(CH_3)_3C_6H_3$ (Schmidbaur, Bublak, Riede & Müller, 1985). The carborane anion acts as an unsymmetrical bridging ligand in a dimer *via* Br7 (see Fig. 1). This structural motif is different from, but similar to, the one-dimensional polymeric structures frequently observed in related silver salts (Xie, Jelínek, Bau & Reed, 1994). The Tl—C_{arene} distances lie in the range of 3.21 (2)–3.35 (2) Å for C3–C8 and 3.27 (2)–3.50 (2) Å for C10–C15. The distances to the arene centers are 2.99 and 3.09 Å, respectively, similar to those reported in $\{[(mes)_2Tl][AlCl_4]\}_2$, $[(mes)_2TlOTeF_5]_2$.mes, $[(mes)_2Tl][B(OTeF_5)_4]$ and $[(mes)_6Tl_4][GaBr_4]_4$ (Frank, Korrell & Reiß, 1995; Noirot, Anderson & Strauss, 1987; Schmidbaur, Bublak, Riede & Müller, 1985), and $(p\text{-}C_6H_4CH_2CH_2)_2$.Tl[$GaCl_4$], a paracyclophane–$Tl^+$ complex (Schmidbaur, Bublak, Huber, Hofmann & Müller, 1989).

A possibly significant feature of one of the coordinated toluene molecules is that in an unconstrained refinement, the methyl group C2 atom is not coplanar with its arene ring but distorted by 0.20 (3) Å, or 7.7 (11)°. Given the dominance of the heavy-atom contributions, apparent distortions in the light atoms can be anticipated. Nevertheless, the distortion is consistent with non-bonded repulsive interactions of the methyl group with nearby Br atoms. The shortest distances are C2···Br12 and C2···Br8^{ii} at 3.61 (2) and 3.89 (1) Å, respectively [symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$]. This distortion may arise because of energetically compensating packing efficiencies elsewhere in the molecular structure.

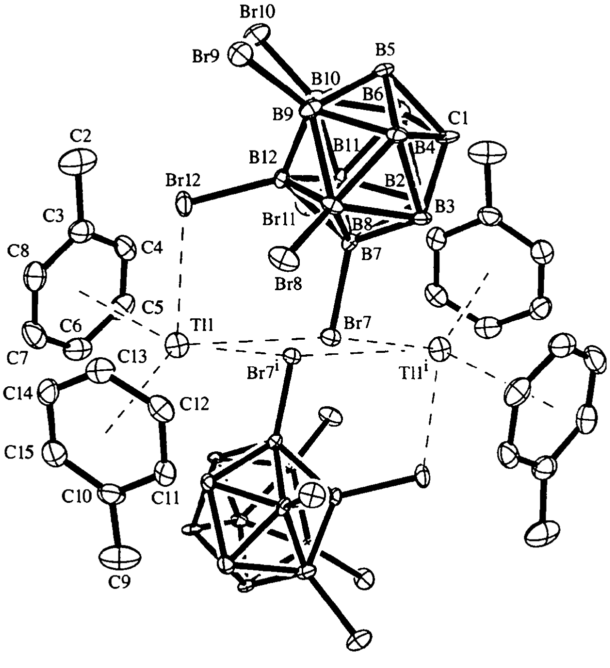


Fig. 1. The molecular structure of $[Tl(C_7H_8)_2](CB_{11}H_6Br_6)$ with the atom-numbering scheme. Ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y, -z$.]

Experimental

A solution of $CsCB_{11}H_6Br_6$ (Jelínek, Plešek, Heřmánek & Štíbr, 1986) in water/methanol was treated with an aqueous solution of excess TlF. The methanol was allowed to evaporate and the aqueous mixture chilled in an ice bath. The bright white precipitate of $TlCB_{11}H_6Br_6$ was collected by filtration and dried. Colorless crystals for diffraction were grown from a toluene solution by vapor diffusion with hexanes. They were placed in Paratone-N oil immediately upon removal from the mother liquor. Upon standing in air, the crystals readily lose toluene to give a bright white amorphous powder.

Crystal data

$[Tl(C_7H_8)_2](CB_{11}H_6Br_6)$
$M_r = 1005.07$
Monoclinic
$P2_1/n$
$a = 9.186\ (2)$ Å
$b = 22.603\ (6)$ Å
$c = 13.685\ (3)$ Å
$\beta = 101.600\ (10)°$
$V = 2783.4\ (11)$ Å^3
$Z = 4$
$D_x = 2.398$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 61 reflections
$\theta = 3.59$–$19.66°$
$\mu = 14.423$ mm^{-1}
$T = 143\ (2)$ K
Prism
0.30 × 0.25 × 0.22 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (Siemens, 1991)
$T_{min} = 0.013$, $T_{max} = 0.042$
4480 measured reflections
3089 independent reflections
1951 reflections with $I > 2\sigma(I)$

$R_{int} = 0.091$
$\theta_{max} = 21.25°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 23$
$l = -13 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: 18.65%

Refinement

Refinement on F^2
$R(F) = 0.044$
$wR(F^2) = 0.082$
$S = 1.034$
3075 reflections
300 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.314$ e Å^{-3}
$\Delta\rho_{min} = -1.287$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Tl1—C3	3.35 (2)	Tl1—C12	3.27 (2)
Tl1—C4	3.26 (2)	Tl1—C13	3.297 (15)
Tl1—C5	3.21 (2)	Tl1—C14	3.361 (14)
Tl1—C6	3.281 (14)	Tl1—C15	3.462 (15)
Tl1—C7	3.308 (14)	Tl1—Br12	3.393 (2)
Tl1—C8	3.336 (14)	Tl1—Br7	3.421 (2)
Tl1—C10	3.50 (2)	TL1—Br7^{i}	3.592 (2)
Tl1—C11	3.41 (2)		

Symmetry code: (i) $-x, -y, -z$.

The data were collected to $\theta_{\max}$ of 21.25°, the practical limit for useful data collection. Beyond this there was only minor diffraction which presumably held information only about the heavy atoms and whose collection would have compromised the crystal stability. Numerical methods of absorption correction were not available; the crystal had been mounted in Paratone-N oil and so the required indexing of crystal faces was not possible. No geometrical restraints were applied to the toluene rings or other parts of the structure. All non-H atoms were refined anisotropically with appropriate thermal motion restraints. The H atoms were positioned and included in the refinement using the appropriate options available in *SHELXL*93 (Sheldrick, 1993). The largest feature in the final difference Fourier map was located 1.29 Å from the Tl atom.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1128). Services for accessing these data are described at the back of the journal.

References

Bolskar, R. D., Mathur, R. S. & Reed, C. A. (1996). *J. Am. Chem. Soc.* **118**, 13093–13094.

Frank, W., Korrell, G. & Reiß, G. J. (1995). *Z. Anorg. Allg. Chem.* **621**, 765–770.

Jelínek, T., Plešek, J., Heřmánek, S. & Štíbr, B. (1986). *Collect. Czech. Chem. Commun.* **51**, 819–829.

Liston, D. J., Lee, Y. J., Scheidt, W. R. & Reed, C. A. (1989). *J. Am. Chem. Soc.* **111**, 6643–6648.

Noirot, M. D., Anderson, O. P. & Strauss, S. H. (1987). *Inorg. Chem.* **26**, 2216–2223.

Reed, C. A., Xie, Z., Bau, R. & Benesi, A. (1993). *Science*, **262**, 402–404.

Schmidbaur, H., Bublak, W., Huber, B., Hofmann, J. & Müller, G. (1989). *Chem. Ber.* **122**, 265–270.

Schmidbaur, H., Bublak, W., Riede, J. & Müller, G. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 414–415.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1991). *XEMP. Program for Empirical Absorption Correction.* Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Xie, Z., Bau, R. & Reed, C. A. (1995). *Inorg. Chem.* **34**, 5403–5404.

Xie, Z., Jelínek, T., Bau, R. & Reed, C. A. (1994). *J. Am. Chem. Soc.* **116**, 1907–1913.

Xie, Z., Manning, J., Reed, R. W., Mathur, R., Boyd, P. D. W., Benesi, A. & Reed, C. A. (1996). *J. Am. Chem. Soc.* **118**, 2922–2928.