Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Octakis(μ_3-*tert*-butylthiolato)bis(*tert*-butylthiolato)hexakis(1-methylpyrrolidin-2-one)-μ_6-sulfido-hexabarium(II)

Ray J. Butcher[a]* and Andrew P. Purdy[b]

[a]Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, and [b]Chemistry Division Code 6120, Naval Research Laboratory, Washington, DC 20375-5342, USA

Correspondence e-mail: butcher@harker.nrl.navy.mil

Received 28 October 2005
Accepted 15 December 2005
Online 20 January 2006

Key indicators

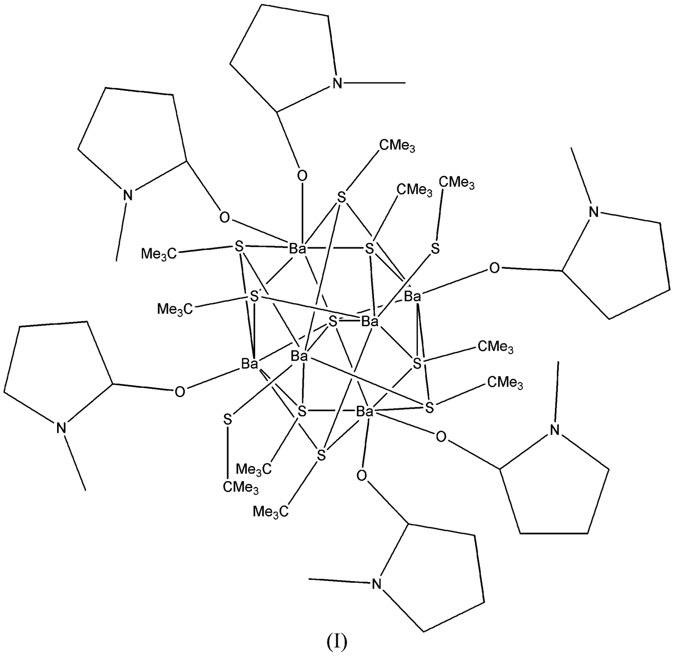
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.017 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.082
Data-to-parameter ratio = 27.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Ba_6(C_4H_9S)_{10}S(C_5H_9NO)_6]$, possessing twofold symmetry, contains a central μ_6-sulfido atom surrounded by six Ba atoms in an almost perfect octahedron. Of the six Ba atoms, two are seven-coordinate with an S_5O_2 donor set, while four are six-coordinate. Two of these have S_5O and two have S_6 donor sets. There are six 1-methyl-2-pyrrolidone donor molecules, two each coordinated to two Ba atoms and one each coordinated to two other Ba atoms.

Comment

There have been numerous examples of high nuclearity transition metal clusters encapsulating S (Allen, 2002). Such SM_6 clusters have been reported for Fe (Zhang *et al.*, 2002, 2003, 2004; Zuo *et al.*, 2003; Osterloh *et al.*, 1999; Ohki *et al.*, 2003), Cu (Wu, *et al.*, 1988; Marsh, 1997; Hu, 2001; Lin *et al.*, 2000*a*; Chen *et al.*, 2003; Tang *et al.*, 1993), Co (Shu *et al.*, 1991), Zr (Fenske *et al.*, 1991) and Ag (Chen *et al.*, 2004; Lin *et al.*, 1997; Matsumoto *et al.*, 2000; Lin *et al.*, 2000*b*; Jin *et al.*, 1996), while SM_8 clusters have been reported for Rh (Vidal *et al.*, 1978) and Cu (Lin *et al.*, 1999; Huang *et al.*, 1991; Dehnen & Fenske, 1996, Liu *et al.*, 1995; Fenske *et al.*, 2004). With the exception of one report of an SLi$_8$ cluster (Banister *et al.*, 1988), there has been no report of an SM_x cluster involving a non-transition metal.



(I)

The title compound, (I), crystallized out of a reaction medium containing barium *tert*-butylsulfide, 1-methyl-2-

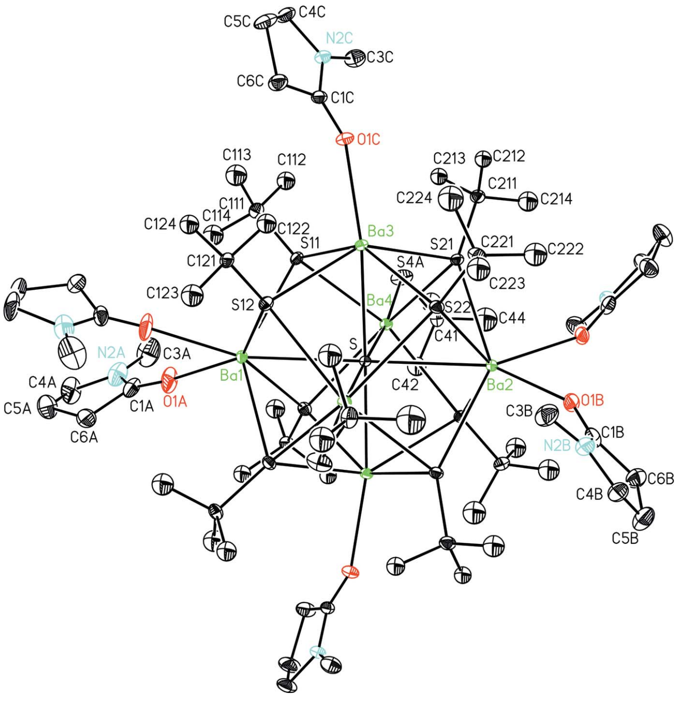


Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 20% probability level. H atoms have been omitted for clarity.

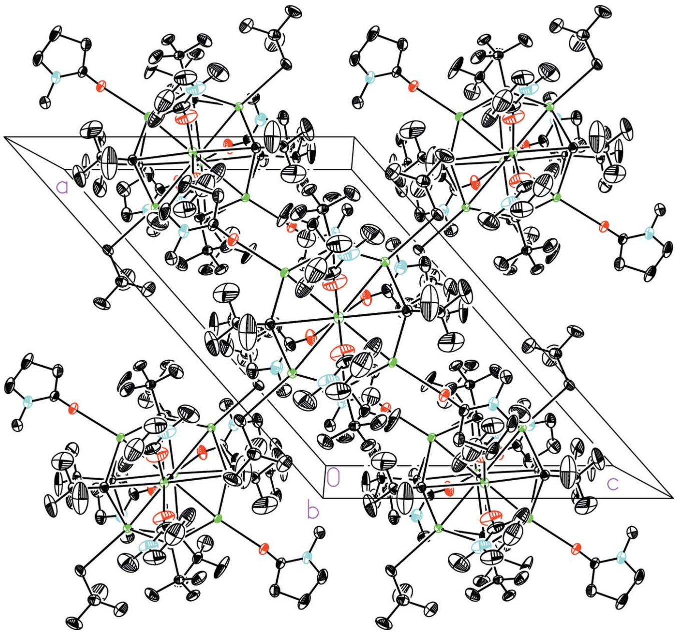


Figure 2
The molecular packing of the title compound viewed along the *b* axis. H atoms have been omitted for clarity.

pyrrolidone (NMP) and C_6D_6 over a period of 6.5 years. The molecule has crystallographically imposed twofold symmetry with Ba1, Ba2 and the central S on a twofold axis. The coordination spheres for both Ba1 and Ba2 are similar, both being seven-coordinate with an S_5O_2 donor set, while Ba3 and Ba4 are both six-coordinate with S_5O and S_6 donor sets, respectively. Of the ten *t*-butylsulfide ligands, eight contain triply bridging S donors, while two are terminally coordinated. There are six 1-methyl-2-pyrrolidone donor molecules coordinated to four of the six Ba atoms. For the central S atom, the six Ba—S distances range from 3.1011 (3) to 3.279 (4) Å with an average of 3.20 (7) Å. The Ba—S distances for the triply bridging S donors range from 3.1389 (18) to 3.2901 (15) Å with an average of 3.209 Å. The terminal Ba—S distance is 3.1258 (13) Å. For the 1-methyl-2-pyrrolidone ligands, the Ba—O distances range from 2.693 (4) to 2.732 (2) Å with an average of 2.707 (18) Å. The six Ba atoms and the central S form an almost perfect octahedron, the maximum deviation of the Ba—S—Ba angles being 0.65 (5).

Experimental

$Ba(SCMe_3)_2$ (Purdy *et al.*, 1997) was dissolved in 1-methyl-2-pyrrolidone containing about 10% C_6D_6 and a drop of trimethylsilane and sealed in an NMR tube. After 6.5 years, a mass of colorless crystals was discovered in the NMR tube. The crystals were sealed in thin-walled glass capillaries.

Crystal data

$[Ba_6(C_4H_9S)_{10}S(C_5H_9NO)_6]$
$M_r = 2340.60$
Monoclinic, $C2$
$a = 21.0316$ (11) Å
$b = 21.7686$ (11) Å
$c = 15.2669$ (8) Å
$\beta = 131.391$ (1)°
$V = 5243.7$ (5) Å^3
$Z = 2$

$D_x = 1.482$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7746 reflections
$\theta = 2.6$–29.2°
$\mu = 2.48$ mm^{-1}
$T = 296$ (2) K
Chunk, colourless
0.4 × 0.3 × 0.2 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.498$, $T_{\max} = 0.609$
21162 measured reflections

11503 independent reflections
9871 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 29.3°$
$h = -27 \rightarrow 25$
$k = -29 \rightarrow 29$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.082$
$S = 1.05$
11503 reflections
416 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 14.7453P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Absolute structure: Flack (1983), with 4126 Friedel pairs
Flack parameter: 0.45 (2)

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry with C—H distances of 0.96 Å and $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$, but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.96–0.97 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. There are several disordered components in this structure: (*a*) S4 is disordered over two positions (S4*A* and S4*B*) with occupancies of 0.81 (2) and 0.19 (2); (*b*) the *tert*-butyl group attached to S11 is disordered over two conformations with occupancies of

0.64 (1) and 0.36 (1); (*c*) the *tert*-butyl group attached to S21 is disordered over two conformations with occupancies of 0.55 (2) and 0.45 (2). Both *tert*-butyl groups were restrained to be tetrahedral. The value of the Flack parameter (Flack, 1983) suggests inversion twinning.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

APP acknowledges ONR for funding.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Banister, A. J., Clegg, W. & Gill, W. R. (1988). *Chem. Commun.* pp. 131–133.

Bruker (1998). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, J.-X., Xu, Q.-F., Zhang, Y., Chen, Z.-N., & Lang, J.-P. (2004). *J. Organomet. Chem.* **689**, 1071–1077.

Chen, Y.-B., Li, Z.-J., Qin, Y.-Y., Kang, Y., Cheng, J.-K., Hu, R.-F., Wen, Y.-H. & Yao, Y.-G. (2003). *Inorg. Chem. Commun.* **6**, 405–407.

Dehnen, S. & Fenske, D. (1996). *Chem. Eur. J.* **2**, 1407–1416.

Fenske, D., Grissinger, A., Loos, M. & Magull, J. (1991). *Z. Anorg. Allg. Chem.* **598–599**, 121–128.

Fenske, D., Rothenberger, A. & Fallah, M. S. (2004). *Z. Anorg. Allg. Chem.* **630**, 943–947.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Huang, Z.-X., Lu, S.-F., Huang, J.-Q., Wu, D.-M. & Huang, J.-L. (1991). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **10**, 213–217.

Hu, S.-Z. (2001). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **20**, 151–155.

Jin, X., Tang, K., Liu, W., Zeng, H., Zhao, H., Ouyang, Y. & Tang, Y. (1996). *Polyhedron*, **15**, 1207–1211.

Lin, P., Wu, X., Chen, L., Du, W. & Zheng, Y. (1999). *J. Chem. Crystallogr.* **29**, 581–586.

Lin, P., Wu, X., Chen, L., Wu, L. & Du, W. (2000*b*). *J. Chem. Crystallogr.* **30**, 55–60.

Lin, P., Wu, X., Zhang, W., Guo, J., Sheng, T., Wang, Q. & Lu, J. (1997). *Chem. Commun.* pp. 1349–1350.

Lin, P., Wu, X.-T., Chen, L., Wu, L.-M., & Du, W.-X. (2000*a*). *Polyhedron*, **19**, 2189–2193.

Liu, C. W., Stubbs, T., Staples, R. J. & Fackler, J. P. Jr (1995). *J. Am. Chem. Soc.* **117**, 9778–9779.

Marsh, R. E. (1997). *Acta Cryst.* B**53**, 317–322.

Matsumoto, K., Tanaka, R., Shimomura, R. & Nakao, Y. (2000). *Inorg. Chim. Acta*, **304**, 293–296.

Ohki, Y., Sunada, Y., Honda, M., Katada, M. & Tatsumi, K. (2003). *J. Am. Chem. Soc.* **125**, 4052–4053.

Osterloh, F., Sanakis, Y., Staples, R. J., Munck, E. & Holm, R. H. (1999). *Angew. Chem. Int. Ed.* **38**, 2066–2068.

Purdy, A. P., Berry, A. D. & George, C. F. (1997). *Inorg. Chem.* **36**, 3370–3375.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Shu, T. L., Xiang, H., Qi, W. L. & Zhang, W. T. (1991). *Chin. Chem. Lett.* **2**, 335–337.

Tang, K., Xia, T., Jin, X. & Tang, Y. (1993). *Polyhedron*, **12**, 2895–2898.

Vidal, J. L., Fiato, R. A., Cosby, L. A. & Pruett, R. L. (1978). *Inorg. Chem.* **17**, 2574–2582.

Wu, X., Wang, B., Zheng, Y. & Lu, J. (1988). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **7**, 47–49.

Zhang, Y. & Holm, R. H. (2003). *J. Am. Chem. Soc.* **125**, 3910–3920.

Zhang, Y. & Holm, R. H. (2004). *Inorg. Chem.* **43**, 674–682.

Zhang, Y., Zuo, J.-L., Zhou, H.-C. & Holm, R. H. (2002). *J. Am. Chem. Soc.* **124**, 14292–14293.

Zuo, J.-L., Zhou, H.-C. & Holm, R. H. (2003). *Inorg. Chem.* **42**, 4624–4631.