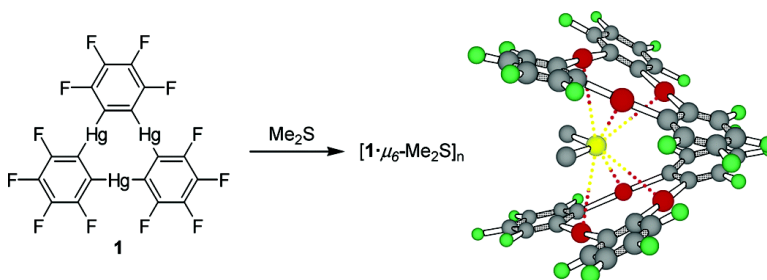


Hexacoordination of a Dimethyl Sulfide Molecule

Mitsukimi Tsunoda, and Francois P. Gabba

J. Am. Chem. Soc., **2003**, 125 (35), 10492-10493 • DOI: 10.1021/ja036197n • Publication Date (Web): 08 August 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

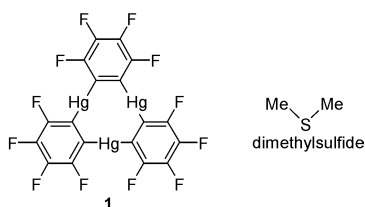
Hexacoordination of a Dimethyl Sulfide Molecule

Mitsukimi Tsunoda and François P. Gabbaï*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received May 16, 2003; E-mail: francois@tamu.edu

Polyfunctional organomercurials constitute a remarkable class of Lewis acidic hosts that have proved useful in the domain of molecular recognition^{1–3} and catalysis.⁴ At the fundamental level, advances made in this field of chemistry have led to the discovery of hypercoordinated anion complexes in which the anion is four-,⁵ five-,^{3,6} and sometimes even six-coordinate.^{3,7} Realization of such unusually high coordination number is likely assisted by the negative charge of the anionic guest. Hence, neutral guest molecules typically display lower coordination numbers. In addition to two-coordinate organic carbonyl, nitrile, sulfoxide, and cyclic ether complexes formed with bidentate 1,2-bis(chloromercurio)benzene receptors,^{1b,8} three-,^{9,10} and rarely four-coordinate^{1b} complexes can be isolated when macrocyclic polydentate organomercurials are employed. As part of our continuing interest in the chemistry of trimeric perfluoro-*ortho*-phenylene mercury (**1**)¹¹ as a receptor for neutral substrates including arenes,^{9,12} we have turned our attention to the case of thioethers and report on the preparation and structural characterization of a supramolecular complex that features a hexacoordinated dimethyl sulfide molecule.



Slow concentration of a dimethyl sulfide solution of **1** yields $[1 \cdot (\text{Me}_2\text{S})_2(\mu_3\text{-Me}_2\text{S})_2]$ (**2**), in which four molecules of dimethyl sulfide are simultaneously bound to the trifunctional Lewis acid **1**. Compound **2** crystallizes in the triclinic space group *P*-1 with two molecules in the asymmetric unit.¹³ In both molecules, which approach *C*₂ symmetry, two of the dimethyl sulfide molecules act as terminal ligands and coordinate to a single mercury atom via S···Hg interactions of av 3.30 Å (Figure 1). The other two dimethyl sulfide molecules are located above and below the plane of the trinuclear complex and interact simultaneously with the three mercury atoms. In each case, the dimethyl sulfide molecule forms one short Hg···S interaction (av 3.24 Å) and two longer ones (av 3.47 Å). The range of these Hg···S interactions, however, is narrow so that the dimethyl sulfide can be regarded as symmetrically coordinated to the three mercury atoms. While there is no precedent for triply bridging dialkyl sulfide molecule, we note that complexes featuring a μ_3 -water molecule were reported by Hawthorne.¹⁴ In **2**, the structure of the triply coordinated dimethyl sulfide molecules is close to that described for the free molecule in the gas phase.¹⁵ Although no previous structural data is available for adducts involving a dialkyl sulfide and an organomercurial,¹⁶ the length of the Hg···S linkages observed in **2** remains within the sum of the van der Waals radii for sulfur ($r_{\text{vdw}} = 2.03$ Å)¹⁷ and mercury ($r_{\text{vdw}} = 1.73$ – 2.00 Å),¹⁸ indicating the presence of secondary interactions. These secondary interactions are shorter than those observed in the

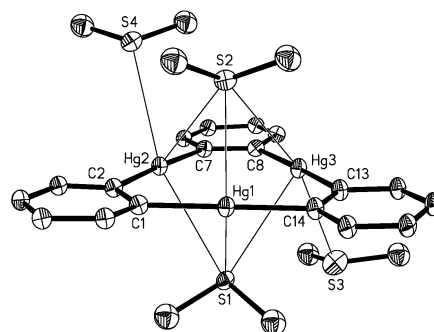


Figure 1. Molecular structure of one of the two molecules present in the asymmetric unit of **2** (30% ellipsoid); F and H atoms omitted for clarity. Selected bond lengths [Å] Hg(1)–C(1) 2.07(2), Hg(1)–C(14) 2.10(2), Hg(1)–S(2) 3.198(7), Hg(1)–S(1) 3.269(7), Hg(2)–C(7) 2.07(2), Hg(2)–C(2) 2.08(2), Hg(2)–S(4) 3.371(7), Hg(2)–S(2) 3.424(8), Hg(2)–S(1) 3.452(6), Hg(3)–C(8) 2.05(2), Hg(3)–C(13) 2.05(2), Hg(3)–S(3) 3.229(9), Hg(3)–S(1) 3.499(7), Hg(3)–S(2) 3.508(7).

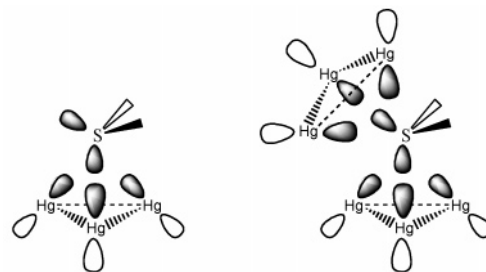


Figure 2. Proposed orbital diagram depicting the bonding interaction between Me₂S and the Hg centers of **1** in **2** (left) and **3** (right).

structure of $[\text{tht} \cdot \text{HgCl}_2]$ (3.89 Å) but remain longer than the primary Hg–S bond (2.40 Å) found in this adduct.¹⁹ The small dihedral angles of 33.9–38.4° formed between the plane containing the three mercury atoms and the plane containing the sulfur and carbon atoms of the triply coordinated dimethyl sulfide molecules suggest that only one of the sulfur atom lone pairs participates in bonding with the neighboring mercury atoms. Hence, on the basis of this structural analysis, we propose that each triply bridging dimethyl sulfide molecule is held by a 4c-2e bond involving overlap of a sulfur lone pair with the three vacant 6p orbitals of the juxtaposed mercury centers (Figure 2). This situation is comparable to that encountered in complexes featuring bridging phosphines.²⁰ Finally, the S(1)–Hg(2)–S(4) (162.22(10)°) and S(2)–Hg(3)–S(3) (163.15(12)°) angles are close to linear, thus suggesting participation of a unique Hg(2) and Hg(3) 6p orbital in the binding of the two trans dimethyl sulfide ligands at these metal centers.

Crystals of **2** become quickly opaque when removed from the mother liquor. Elemental analysis carried out on the resulting material indicates the loss of exactly 3 equiv of dimethyl sulfide, thus suggesting the formation of a stable 1:1 adduct $[1 \cdot \text{Me}_2\text{S}]$. While the crystallinity of the resulting material was not sufficient for X-ray analysis, addition of excess dimethyl sulfide to a solution of **1** in

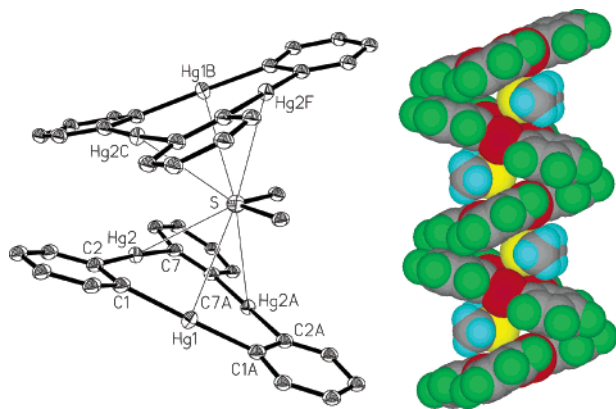


Figure 3. (Left) View showing the coordination of the sulfur atom in the structure of **3** (50% ellipsoid); F and H atoms omitted for clarity. Selected bond lengths [Å]: Hg(1)–C(1) 2.04(2), Hg(1)–S 3.571(3), Hg(2)–C(7) 2.09(2), Hg(2)–C(2) 2.09(2), Hg(2)–S 3.543(7). (Right) Space filling view of a portion of a stack in the structure of **3**. Color code: C, gray; H, blue; F, green; and Hg, red; S, yellow.

1,2-dichloroethane followed by slow evaporation led to the crystallization of an adduct of identical stoichiometry which has been identified as $[1 \cdot \mu_6\text{-Me}_2\text{S}]_n$ (**3**). Compound **3** is stable at room temperature but loses dimethyl sulfide above 100 °C as indicated by TGA analysis.

The structure of compound **3** reveals extended stacks that run parallel to one another.¹³ Each stack has crystallographically imposed C_2 symmetry and consists of staggered molecules of **1** that sandwich molecules of dimethyl sulfide (Figure 3). The molecules of **1** deviate slightly from planarity and adopt a propeller conformation. Within each stack, the trinuclear cores of the successive molecules of **1** are not parallel and form a dihedral angle of 45.4°. This arrangement results in the generation of pockets which are occupied by the dimethyl sulfide molecules. As a result of this unique arrangement, the sulfur atom of the dimethyl sulfide molecule interacts simultaneously with the six mercury atoms provided by the two juxtaposed molecules of **1** (Figure 3). The resulting Hg(1)···S and Hg(2)···S distances of 3.571(3) and 3.543(7) Å, are slightly longer than those observed in **2** for the triply coordinated dimethyl sulfide molecules but remain within the sum of the van der Waals radii of the two elements. The Hg₃ centroid–S–Hg₃ centroid angle of 135.6° only slightly exceed the value of 125° typically observed for the metal–S–metal angle found in complexes featuring a μ_2 -dimethyl sulfide ligand bridging two independent metal moieties.²¹ This observation indicates that the sulfur lone pairs point toward the center of each neighboring molecules of **1**. Hence, elaborating on the bonding description provided for **2**, we propose that the dimethyl sulfide molecule participates in two distinct 4c–2e bonds involving each of its lone pairs and sets of three 6p mercury orbitals (Figure 2). The dihedral angle of 22.7° formed between the plane containing the three mercury atoms and the plane containing the sulfur and carbon atoms of the dimethyl sulfide molecules lends support to this proposal. The structure of **3** is reminiscent of that of the anionic complex $[1 \cdot \text{SCN}]^-$ reported by Shur.²² This anionic complex adopts an extended structure which consists of alternating molecules of **1** and SCN[−] ions. Unlike in neutral **3**, the sulfur atoms of the SCN[−] ion in $[1 \cdot \text{SCN}]^-$ interact unsymmetrically with the mercury atoms of the neighboring molecules of **1** with which it forms four short Hg···S bonds that range from 3.06(1) to 3.36(1) Å and two long bonds of 3.74(1) and 3.87(1) Å whose length approaches the limit for the involvement of dative interactions.

In conclusion, we report the structure of a supramolecular complex which features a μ_6 -dimethyl sulfide molecule. This represents

an unusually high coordination mode for a neutral dialkyl sulfide molecule which typically serves as a terminal or μ_2 -bridging ligand.

Acknowledgment. This work was supported by the U.S. Army Medical Research and Materiel Command and the Department of Chemistry at Texas A&M University. The purchase of the X-ray diffractometer was made possible by a grant from the National Science Foundation (CHE-98 07975).

Supporting Information Available: Experimental procedures (PDF), X-ray structure data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267–276. (b) Wuest, J. D. *Acc. Chem. Res.* **1999**, *32*, 81–89.
- (2) Shubina, E. S.; Tikhonova, I. A.; Bakmutova, E. V.; Dolgushin, F. M.; Antipin, M. Y.; Bakmutov, V. I.; Sivaev, I. B.; Teplitskaya, L. N.; Chizhevsky, I. T.; Pisareva, I. V.; Bregadze, V. I.; Epstein, L. M.; Shur, V. B. *Chem. Eur. J.* **2001**, *7*, 3783–3790.
- (3) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Struchkov, Yu. T.; Yanovsky, A. I.; Tikhonova, I. A.; Shur, V. B. *J. Organomet. Chem.* **1997**, *536*, 413–424 and references therein.
- (4) (a) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1985**, *107*, 6121–6123. (b) Lee, H.; Diaz, M.; Hawthorne, M. F. *Tetrahedron Lett.* **1999**, *40*, 7651–7655. (c) King, J. B.; Gabbai, F. P. *Organometallics* **2003**, *22*, 1275–1280.
- (5) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410–411.
- (6) Shur, V. B.; Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Volkonsky, A. Yu.; Solodova, E. V.; Panov, S. Yu.; Petrovski, P. V.; Vol'pin, M. E. *J. Organomet. Chem.* **1993**, *443*, C19–C21.
- (7) Lee, H.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **2001**, *123*, 8543–8549.
- (8) Beckwith, J. D.; Tschinkl, M.; Picot, A.; Tsunoda, M.; Bachman, R.; Gabbai, F. P. *Organometallics* **2001**, *20*, 3169–3174 and references therein.
- (9) King, J. B.; Haneline, M. R.; Tsunoda, M.; Gabbai, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 9350–9351 and references therein.
- (10) (a) Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **2002**, *654*, 123–131. (b) Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Starikova, Z. A.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **2000**, *613*, 60–67. (c) Baldamus, J.; Deacon, G. B.; Hey-Hawkins, E.; Junk, P. C.; Martin, C. *Aust. J. Chem.* **2002**, *55*, 195–198.
- (11) Sartori, P.; Golloch, A.; *Chem. Ber.* **1968**, *101*, 2004–2009.
- (12) Haneline, M. R.; Tsunoda, M.; Gabbai, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 3737–3742.
- (13) Crystal data. **2**: C₂₆H₂₄F₁₂Hg₃S₄, M_r = 1294.46, triclinic, space group P-1, a = 14.140(3) Å, b = 14.218(3) Å, c = 18.155(4) Å, α = 98.70(3)°, β = 101.50(3)°, γ = 105.75(3)°, V = 3359.6(12) Å³, Z = 4, ρ_{calcd} = 2.559 g cm^{−3}, Mo Kα radiation (λ = 0.71073 Å), T = 180(2) K, 26882 measured reflections, 10221 unique, R_{int} = 0.0397, μ = 14.009 mm^{−1}, Abs. correction using SADABS, min/max transmission = 0.066 and 1, R₁ (I > 2σ) = 0.0585 for 727 parameters. **3**: C₂₀H₆F₁₂Hg₃S, M_r = 1108.08, orthorhombic, space group Pnna, a = 11.151(2) Å, b = 10.743(2) Å, c = 17.987(4) Å, V = 2154.8(7) Å³, Z = 4, ρ_{calcd} = 3.416 g cm^{−3}, Mo Kα radiation (λ = 0.71073 Å), T = 120(2) K, 12935 measured reflections, 1690 unique, R_{int} = 0.1408, μ = 21.530 mm^{−1}, Abs. correction using SADABS, min./max. transmission = 0.397 and 1, R₁ (I > 2σ) = 0.0702 for 80 parameters.
- (14) Lee, H.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 3058–3060.
- (15) Lijima, T.; Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2564–2567.
- (16) Powell, H. B.; Maung, M. T.; Lagowski, J. J. *J. Chem. Soc.* **1963**, 2484–2487.
- (17) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr., Sect. B.* **1985**, *41*, 274–279.
- (18) (a) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta.* **1980**, *45*, L225–L227. (b) Pyykkö, P.; Straka, M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2489–2493.
- (19) The structure of [tht·HgCl₂] features short intramolecular primary Hg–S bonds and long intermolecular secondary Hg–S interactions: see Brändén, C. I. *Ark. Kemi. Sverige* **1964**, *22*, 495–500.
- (20) (a) Pechmann, T.; Brandt, C. D.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3909–3911. (b) Sauthier, M.; Le Guennic, B.; Deborde, V.; Toupet, L.; Halet, J. F.; Réau, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 228–231.
- (21) (a) Baar, C. R.; Hill, G. S.; Vittal, J. J.; Puddephatt, R. J.; *Organometallics* **1998**, *17*, 32–40. (b) Belforte, A.; Calderazzo, F.; Vitali, D.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1985**, *115*, 125–135.
- (22) Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Gavrilova, A. N.; Saitkulova, L. N.; Shubina, E. S.; Epstein, L. M.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **1996**, *508*, 271–273.

JA036197N