are grateful for helpful discussions with Professors B. Snider (Brandeis), J. Crandall (Indiana), and S. Denmark (Illinois) on the subject of the fluoride-based cyclizations.

Supplementary Material Available: Listings of chemical and spectral data for compounds **17–21** (5 pages). Ordering information is given on any current masthead page.

Synthesis of $(C_5Me_5)Ta(S)_3{}^{2-}$ and the Structure of a Hexagonal-Prismatic $Ta_2Li_4S_6$ Core

Kazuyuki Tatsumi,* Yoshihisa Inoue, and Akira Nakamura*

Department of Macromolecular Science
Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

Roger E. Cramer,* William VanDoorne,† and John W. Gilje

Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

Received September 26, 1988

The attention that has been paid to synthesis and structures of sulfido- and polysulfido-metal complexes derives both from the well-established significance of such compounds in metalloenzymatic catalysis and also from the wealth of their own chemistry. Our attempt to prepare sulfido complexes of pentamethylcyclopentadienyltantalum, Cp*Ta, was prompted by the two motives. One is the beautiful chemistry developed recently from the closely related complexes $Cp'_2Mo_2S_4$[1] and $Cp'_2V_2S_4$ (Cp′ = C_5H_4Me).[2] The other is the EI fragmentation pattern of $Cp^*Ta(SCH_2CH_2S)_2$ which shows sets of peaks associated with $Cp^*Ta(SCH_2CH_2S)(S_2)^+$ and $Cp^*Ta(S_2)_2{}^+$.[3]

Aiming to synthesize relevant disulfido(2−) complexes, we ran a reaction between Cp^*TaCl_4 and 2 equiv of Li_2S_2[4a] in THF, only to find that an uncharacterizable orange-colored gum was formed. However, when the amount of Li_2S_2 was increased by 2–2.5 times we were able to isolate the unexpected title complex **1** which carries three terminal sulfides at a Ta center. Thus, the reaction of Cp^*TaCl_4 with 4–5 equiv of Li_2S_2 in dry THF under Ar gave **1** as light yellow crystals (ca. 50% yield), after evaporation of the solvent, extraction of the residue with benzene, and recrystallization from THF/hexane.[5a] Formation of **1** was also noted when $Cp^*Ta(SCH_2CH_2S)_2$ was treated with 2 equiv of Li_2S_2 in THF, which is an intriguing reaction by itself. Upon introducing a THF solution of $Cp^*Ta(SCH_2CH_2S)_2$ to a THF suspension of Li_2S_2, the color of the solution turned gradually from red to yellow, and, after filtrating off the insoluble yellow residue, **1** (crystals, 42% yield) was readily isolated from the filtrate by concentrating it in vacuo to ca. one-seventh of its original volume.

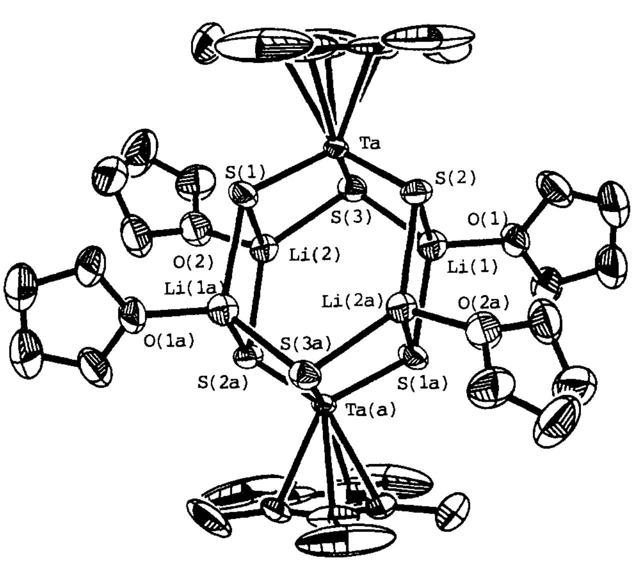
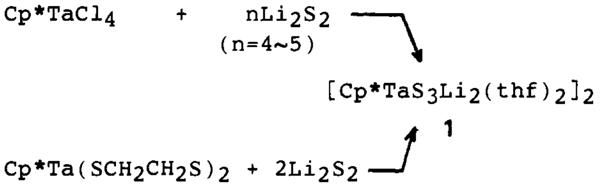


Figure 1. Molecular structure and atom-labeling scheme for $[Cp^*TaS_3Li_2(thf)_2]_2$ (**1**) drawn with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Ta–S(1), 2.270 (2); Ta–S (2), 2.268 (3); Ta–S(3), 2.300 (3); Ta–C(1), 2.48 (1); Ta–C(2), 2.47 (1), Ta–C(3), 2.45 (1); Ta–C(4), 2.46 (1); Ta–C(5), 2.45 (2); Ta–Ta(a), 5.490 (1); Li(1)–S(1a), 2.45 (2); Li(1)–S(2), 2.54 (2); Li(1)–S(3), 2.44 (2); Li(2)–S(1), 2.50 (2); Li(2)–S(2a), 2.49 (2); Li(2)–S(3), 2.44 (2); Li(1)–O(1), 1.96 (2); Li(2)–O(2), 1.90 (2); S(1)–Ta–S(2), 107.1 (1); S(1)–Ta–S(3), 103.4 (1); S(2)–Ta–S(3), 104.1 (1); S(1a)–Li(1)–S(2), 104.7 (6); S(1a)–Li(1)–S(3), 133.1 (7); S(2)–Li(1)–S(3), 92.7 (6); S(1)–Li(2)–S(2a), 104.9 (7); S(1)–Li(2)–S(3), 93.1 (5); S(2a)–Li(2)–S(3), 118.4 (7).



With the stoichiometry of **1** being established, we attempted the reaction between Cp^*TaCl_4 and 3 equiv of Li_2S.[4b] However, isolation of **1** from the resultant red powder[6] has not been successful. Instead, we noticed formation of **1** (ca. 50% yield) when the amount of Li_2S was increased to 5 equiv as in the case of the reaction with Li_2S_2. On the other hand, addition of tetramethylethylenediamine (tmeda) (excess) into a THF solution of **1** afforded a stoichiometric amount of yellow crystalline powder formulated as $Cp^*TaS_3Li_2(tmeda)_2$ **2**.[5b] The sulfide complexes **1** and **2** are moderately air-sensitive and hygroscopic.

Figure 1 shows an ORTEP view of the structure determined for **1** by X-ray crystallography,[7] along with the salient intramolecular

---

† Present address: Department of Chemistry, Calvin College, Grand Rapids, MI 49506.

(1) (a) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064–3071. (b) Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482–5489, and references therein. (c) Wright, L. L.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Ibid.* **1987**, *109*, 282–283. (d) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107–1113. (e) Beck, W.; Danzer, W.; Thiel, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 582–583.

(2) (a) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 7313–7314. (b) Rauchfuss, T. B.; Weatherill, T. D.; Wilson, S. R.; Zebrowski, J. P. *Ibid.* **1983**, *105*, 6508–6509. (c) For $Cp^*{}_2Cr_2S_5$, see: Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *Ibid.* **1982**, *104*, 1765–1766. (d) For $Cp'_4Ti_4S_8O_x$, see: Zank, G. A.; Jones, C. A.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 1886–1891.

(3) Tatsumi, K.; Takeda, J.; Sekiguchi, Y.; Kohsaka, M.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 332–333.

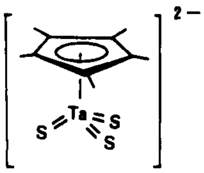
(4) (a) "Li_2S_2" (light yellow powder) was prepared by reaction of lithium metal with elemental sulfur (1:1) in liquid ammonia. This "Li_2S_2" was nearly identical with that prepared from the reaction between $LiEt_3BH$ (Super Hydride) and $^1/_8S_8$ according to their Raman spectra. Further characterization of the lithium sulfide(s) is underway. Before use, the resulting yellow powder was washed by THF under Ar until the filtrate became nearly colorless. See: Letoffe, J. M.; Thourey, J.; Perachon, G.; Bousquet, J. *Bull. Soc. Chim. Fr.* **1976**, 424–426. Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1988**, *27*, 73–80; Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1978**, *35*, 2329–2335. (b) "Li_2S" (yellowish white powder) was prepared similarly from the $Li/^1/_{16}S_8$ reaction system.

(5) (a) $[Cp^*TaS_3Li_2(thf)_2]_2$ **1**: ^1H NMR (100 MHz, THF-d_8) δ 2.10 (s, Cp*); UV (λ_{max} (10^{-3} ϵ_{max}, M^{-1} cm^{-1}), THF) 302 (16.6) nm; Raman (crystals) 619 w, 597 m, 552 w, 434 s (Ta=S), 418 sh, 368 w, 354 w. (b) $Cp^*TaS_3Li_2(tmeda)_2$ **2**: ^1H NMR (100 MHz, C_6D_6) δ 2.49 (s, Cp*), 2.44 (s, $(CH_3)_2NCH_2CH_2N(CH_3)_2$), 2.18 (s, $(CH_3)_2NCH_2CH_2N(CH_3)_2$); UV ($\lambda_{max}$ (10^{-3} ϵ_{max}, M^{-1} cm^{-1}), C_6H_6) 305 (7.2) nm; Raman (crystals) 618 w, 595 w, 552 w, 432 s (Ta=S), 423 sh, 401 m, 350 w. The molecular weight estimated by cryoscopy in benzene is not accurate because of relatively low solubility of **2**, ranging from 500–700 which however might indicate the monomeric nature of **2**.

(6) Characterization of the product(s) is in progress.

0002-7863/89/1511-0782$01.50/0

metrical parameters. A striking feature of the structure is the presence of the novel $Cp^*TaS_3^{2-}$ unit (A) which is the first organometallic species having three terminal sulfides. The known tri(sulfido) complexes are limited to a family of the MS_3E^{n-} anions (E = O, S, Se),[8] and for Ta the occurrence of metal–sulfur double bonds itself is very rare indeed.[9–11] The molecule that most closely resembles A, both geometrically and electronically, is perhaps the trioxorhenium complex, Cp^*ReO_3.[12,13]



A

In the crystal structure, four Li cations link two $Cp^*TaS_3^{2-}$ units where a crystallographic center of symmetry lies in the middle of the two units. The main frame of 1 may be viewed as a distorted hexagonal prism with metal atoms (Ta and Li) and sulfur atoms occupying alternative vertices. Such a prismatic M_6S_6 core also has been found in $(Ph_2PCH_3)_4Ag_4W_2S_8$[14] and $[Fe_6S_6X_6]^{3-}$ (X = Cl, I, SR, OR).[15] Complex 1 extends this limited range of compounds to two more groups of the periodic table and to new types of supporting ligands including the organometallic Cp* group. This suggests that the M_6S_6 cage structure will be found in many more M_xS_y clusters.

The geometry about the two crystallographically independent lithium atoms is basically tetrahedral where each lithium is bonded to three sulfurs and a THF molecule. In the $Ta_2Li_4S_6$ core, the six unique Li–S bond lengths vary from 2.44 (2) to 2.54 (2) Å. The Ta–S distances range from 2.268 (3) to 2.300 (3) Å with the longest being the Ta–S(3) bond. They may be compared with the terminal Ta–S bond lengths of $TaSCl_3(PhSCH_2CH_2SPh)$ (2.204 (5) Å),[9a] $TaS(S_2CNEt_2)_3$ (2.181 (1) Å,[9b] and $[Et_4N]_4[Ta_6S_{17}]$ (2.145 (5)–2.204 (4) Å).[9c] The somewhat longer Ta–S distances observed for 1 have to be interpreted with caution and should not be attributed entirely to the presence of Li–S interactions, because in going from sulfido to tri(sulfido) systems M═S bonds tend to be elongated due to electronic reasons. As a matter of fact, whereas the Ta═S stretching mode of 1 (Raman, 434 cm^{-1}) is at lower frequency than those of $TaSX_3L_2$ (X = Cl, Br) (504–512 cm^{-1}),[9a] it is higher than the A_1 mode stretch of TaS_4^{3-} (424 cm^{-1}).[10c] Thus the tantalum–sulfur double bond character remains strong in the dimeric structure.

Our synthetic study of 1 provides a convenient entry into rare Ta sulfides, and the $Cp^*TaS_3^{2-}$ unit may serve as a potential building block of a wide range of homo- and heteronuclear sulfide clusters.

Acknowledgment. The support of this work at the University of Hawaii by the National Science Foundation, Grant CHE 85-19289, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Complete listings of positional and thermal parameters and bond distances and angles for 1 (44 pages); table of observed and calculated structure factors for 1 (16 pages). Ordering information is given on any current masthead page.

---

[7] Crystal data for 1: crystal size 0.7 × 0.5 × 0.3 mm, monoclinic, space group $C2/c$, $a = 24.879$ (5) Å, $b = 11.501$ (2) Å, $c = 16.669$ (3) Å, $\beta = 99.21$ (1)°, $V = 4708$ (1) Å^3, $\rho_{calcd} = 1.61$ g cm^{-3}, $Z = 4$, μ (Mo Kα) = 4.88 cm^{-1}. Of 5782 reflections collected (Nicolet R diffractometer, 25 °C, scan type $\theta/2\theta$, 4° < 2θ < 55°, scan speed 3.0–29.3°/min), 4775 observed reflections $I > 3\sigma(I)$ were used for the structure determination. An empirical correction for absorption was applied to the data. The structure was solved by direct methods and was refined by subsequent full-matrix least squares where hydrogen atoms were not located and the other atoms except for lithiums were treated anisotropically. $R = 4.3\%$, $R_G = 4.7\%$, GOF = 7.96, $\Delta/\sigma = 0.21$, $\Delta(\rho)_{max} = 0.42$ eÅ^{-3}, $N_o/N_v = 21.2$. All computations used Nicolet SHELXTL PLUS with micro VAX II.

[8] (a) Müller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934–955, and references therein. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635–4642.

[9] (a) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 845–848. (b) Peterson, E. J.; von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1978**, *17*, 1410–1415. (c) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Ibid.* **1985**, *24*, 1706–1713.

[10] For TaS_4^{3-}, see: (a) Crevecoeur, C. *Acta Crystallogr.* **1964**, *17*, 757. (b) Omloo, W. P. F. A. M.; Jellinek, F.; Müller, A.; Diemann, E. *Z. Naturforsch.* **1970**, *B25*, 1302–1303. (c) Müller, A.; Schmidt, K. H.; Tytko, K. H.; Bouwma, J.; Jellinek, F. *Spectrochim. Acta* **1972**, *A28*, 381–391.

[11] The niobium complexes having terminal metal–sulfur bonds are also limited, see: (a) Drew, M. G. B.; Fowles, G. W. A.; Hobson, R. J.; Rice, D. A. *Inorg. Chim. Acta* **1976**, *20*, L35–L36. (b) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1983**, 2251–2256. Drew, M. G. B.; Rice, D. A.; Williams, D. M. *Ibid.* **1985**, 1821–1828. Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358–1359.

[12] Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383–385.

[13] Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313–1314.

[14] Stalick, J. K.; Siedle, A. R.; Mighell, A. D.; Hubbard, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2903–2907.

[15] Kanatzidis, M. G.; Hagen, W. R.; Dunham, W. R.; Lester, R. K.; Coucouvanis, D. *J. Am. Chem. Soc.* **1985**, *107*, 953–961.

A New Class of Endoglycosidase Inhibitors. Studies on Endocellulases

Louis J. Liotta,[†] Ronald C. Bernotas,[†] David B. Wilson,[‡] and Bruce Ganem*[,†]

Department of Chemistry, Baker Laboratory
Section of Biochemistry, Molecular and
Cellular Biology, Cornell University
Ithaca, New York 14853

Received August 19, 1988

Although the study of glycosidases dates back to the time of Liebig and Wohler, relatively little is known about the mechanisms and structures of these important enzymes.[1,2] In fact lysozyme remains the only glycosidase for which detailed structural information is available.[2] Recent interest in the naturally occurring exoglycosidase inhibitors 1 and 2 (Chart I) has led to the rational design of other monosaccharide analogues.[3–6] Unfortunately 1 and 2 have no effect on endoglycosidases like lysozyme, chitinase, and cellulase, which bind and cleave randomly at the interior of polysaccharides. It was intriguing to speculate whether oligosaccharides containing a strategically positioned azasugar residue might inhibit endoglycosidases.[7] Here we describe an unusual new reaction of organomercurials leading to the synthesis of oligosaccharides 3–5 (Chart I) which competitively inhibit β-1,4-endoglucanases from the cellulolytic bacterium *Thermomonospora fusca*.

The $NaBH_4$-O_2-DMF reductive oxygenation of mercurial 6 to alcohol 9, a key step in our published syntheses of 1 and 2,[8,9] also afforded an unusual byproduct 11 (Scheme I, 5% yield) in which the C4-benzyl ether was selectively removed with concomitant

---

[†] Department of Chemistry, Baker Laboratory.

[‡] Section of Biochemistry, Molecular and Cellular Biology.

[1] Liebig, J.; Wohler, F. *Ann. Pharmazie* **1837**, *21*, 96.

[2] Kirby, A. J. *CRC Crit. Rev. Biochem.* **1987**, *22*, 283.

[3] Lalegerie, P.; Legler, G.; Yon, J. M. *Biochimie* **1982**, *64*, 977.

[4] Schmidt, D. D.; Frommer, W.; Muller, L.; Truscheit, E. *Naturwissenschaften* **1979**, *66*, 584.

[5] (a) Withers, S. G.; Street, I. P.; Bird, P.; Dolphin, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7530. (b) Withers, S. G.; Rupitz, K.; Street, I. P. *J. Biol. Chem.* **1988**, *263*, 7929.

[6] Tong, M. K.; Ganem, B. *J. Am. Chem. Soc.* **1988**, *110*, 312.

[7] Asp or Glu residues are presumably involved in either mono- or bilateral enzymatic catalysis (see ref 2). The role of strain has also been probed: Secemski, I. I.; Lienhard, G. E. *J. Am. Chem. Soc.* **1971**, *93*, 3549.

[8] Bernotas, R. C.; Ganem, B. *Tetrahedron Lett.* **1985**, *26*, 1123.

[9] Hamana, H.; Ikota, N.; Ganem, B. *J. Org. Chem.* **1987**, *52*, 5492.

0002-7863/89/1511-0783$01.50/0