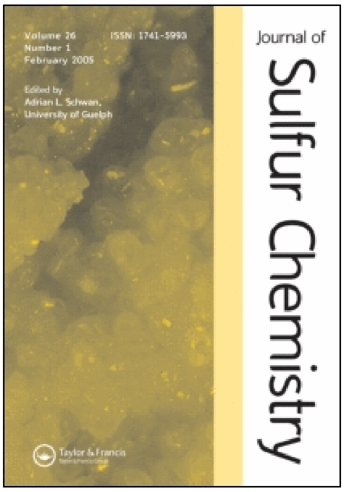


Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Synthesis and structural characterization of a mixed aggregate containing a lithium thiolate and a lithium amide

Kei Goto[a]; Yusuke Takahashi[a]; Takayuki Kawashima[a]
[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, Japan

To cite this Article Goto, Kei , Takahashi, Yusuke and Kawashima, Takayuki(2009) 'Synthesis and structural characterization of a mixed aggregate containing a lithium thiolate and a lithium amide', Journal of Sulfur Chemistry, 30: 3, 365 — 369

To link to this Article: DOI: 10.1080/17415990903026339

URL: http://dx.doi.org/10.1080/17415990903026339

Journal of Sulfur Chemistry
Vol. 30, Nos. 3–4, June–August 2009, 365–369

Synthesis and structural characterization of a mixed aggregate containing a lithium thiolate and a lithium amide

Kei Goto*[†], Yusuke Takahashi and Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, Japan

(*Received 21 February 2009; final version received 5 April 2009*)

This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

The mixed aggregate $Ar_3CSLi{\cdot}(Me_3Si)_2NLi{\cdot}2THF$ (**3**) (Ar = 2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl) containing a lithium thiolate and a lithium amide was synthesized, the crystallographic analysis of which revealed its structure as containing an unfused SLiNLi four-membered ring with short S−Li distances.

Keywords: lithium thiolates; lithium amides; mixed aggregates; X-ray crystallographic analysis; bowl-shaped molecules

1. Introduction

It has been well known that many lithium reagents form mixed aggregates with other organolithium compounds or inorganic lithium salts (*1–4*). Because of the importance and utility of mixed aggregates in organic chemistry, extensive studies have been performed on their synthesis and structures. Lithium organochalcogenates are important reagents for the synthesis of a variety of metal chalcogenolato complexes (*5–11*). For the past two decades, the structural chemistry of lithium organothiolates has been attracting growing attention as demonstrated by the increase of crystallographically characterized compounds of this class. However, there have been only a limited number of examples of mixed aggregates containing lithium organothiolates and other lithium reagents (*12–15*). Veith *et al.* reported the synthesis and crystal structure of compound **1** bearing a N(Li)−Si−C≡C−C=C−SLi fragment (Figure 1) prepared by dilithiation of $[(2\text{-}C_4H_3S)SiMe_2]_2NH$ via ring opening of the thiophene ring, which has been the only example of a mixed aggregate of a lithium thiolate and a lithium amide (*13*). In connection with our studies on the development of novel sulfur compounds bearing a bowl-shaped framework (*16–20*), we report here the synthesis and structural characterization of a mixed aggregate of $LiSR/LiNR'_2$ type.

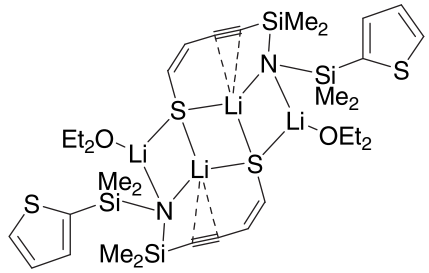
---

*Corresponding authors. Emails: goto@chem.titech.ac.jp; takayuki@chem.s.u-tokyo.ac.jp

[†] Present address: Interactive Research Center of Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan.

ISSN 1741-5993 print/ISSN 1741-6000 online

DOI: 10.1080/17415990903026339
http://www.informaworld.com

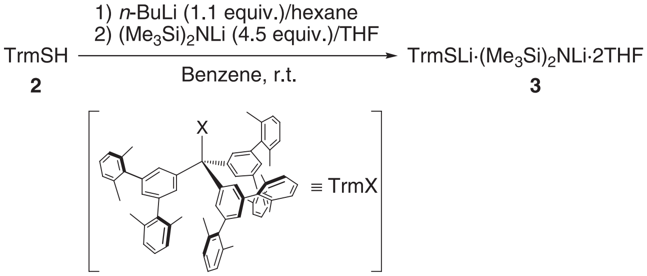


1

Figure 1. Mixed aggregate $[(2\text{-}C_4H_3S)SiMe_2N(Li)SiMe_2C{\equiv}CCH{=}CHSLi{\cdot}OEt_2]_2$ (**1**).

2. Results and discussion

We previously reported the synthesis of thiol **2** bearing a bowl-shaped triarylmethyl substituent (denoted as Trm hereafter) (*17*). The reaction of **2** with *n*-BuLi in benzene followed by treatment with a tetrahydrofuran (THF) solution of $(Me_3Si)_2NLi$ afforded the mixed aggregate $TrmSLi{\cdot}(Me_3Si)_2NLi{\cdot}2THF$ (**3**) (Scheme 1), which was isolated as colorless crystals by recrystallization from benzene/THF.



Scheme 1.

X-ray crystallographic analysis established the structure of **3** containing the thiolate unit, TrmSLi, and the amide unit, $(Me_3Si)_2NLi$, in the 1:1 ratio (Figure 2). There is a SLiNLi four-membered core in this mixed aggregate, and each lithium atom is coordinated by one THF molecule. Regarding the compounds bearing a SLiNLi ring system, only a limited number of crystal structures have been reported to date, in all of which the SLiNLi ring is incorporated within multi-fused ring systems (*13, 21, 22*). This is the first example of the crystallographic analysis of a compound bearing an unfused SLiNLi ring system. The sulfur atom adopts a distorted pyramidal geometry, the sum of the bond angles being 333.4°. The lithium atoms are surrounded in an almost undistorted trigonal planar arrangement by the sulfur, nitrogen, and THF oxygen atoms with the sum of angles of 359.7° for both lithium atoms. The lithium–sulfur distances are 2.338(7) and 2.357(7) Å for Li(1)−S(1) and Li(2)−S(1), respectively, while the S(1)−C(1) distance is 1.854(3) Å. These lithium–sulfur distances, especially the Li(1)−S(1) distance, are significantly shorter than the reported values for $Ph_3CSLi{\cdot}PMDTA$ (2.412(7) Å), $Ph_3CSLi{\cdot}$(12-crown-4) (2.399(4) Å), and $[Ph_3CSLi{\cdot}2THF]_2$ (2.466(5) and 2.494(5) Å) (PMDTA = N, N, N', N'', N''-pentamethyldiethylenetriamine) (*10*). The short Li−S bond lengths in **3** are considered to result from the lower coordination number at lithium. It was reported that, in the crystal structure of $[(Me_3Si)_3CSLi{\cdot}1.5THF]_2$, the distances between sulfur and three-coordinate lithium (2.34 Å

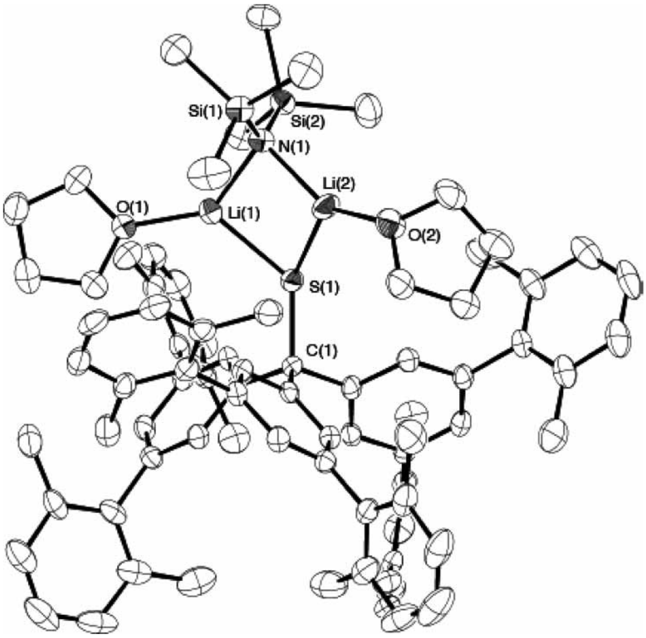


Figure 2. ORTEP drawing of **3** (50% probability). Hydrogen atoms are omitted for clarity.

(average)) are much shorter than those involving four-coordinate lithium (2.49 Å (average)) (*8*). The Li(1)$\cdots$Li(2) distance (2.692(9) Å) in **3** falls between the values observed in dimeric lithium thiolates (RSLi)$_2$ (*7*) and those in dimeric lithium amides (R$_2$NLi)$_2$ (*23*, *24*). The SLiNLi four-membered ring of **3** deviates from planarity and there is a considerable fold angle (149.7°) along the Li$\cdots$Li axis. In the crystal structure of compound **1** reported by Veith *et al.*, two SLiNLi rings are connected to each other to build up a ladder-like structure (*13*). The S–Li bond lengths (2.52 Å (average)) and Li$\cdots$Li distances (2.82 Å (average)) in the SLiNLi rings of **1** are longer than the corresponding values of **3** observed in the present study.

3. Conclusion

The mixed aggregate **3** containing a lithium alkanethiolate and a lithium amide was synthesized by use of the bowl-shaped triarylmethanethiol **2**. X-ray crystallographic analysis established the structure of **3** as containing an unfused SLiNLi four-membered ring with short S–Li distances. Further investigations on the conversion of **3** to other metal thiolates are currently underway.

4. Experimental

All reactions and manipulations were performed under argon atmosphere. Melting points were determined on a Yanaco micro melting point apparatus and uncorrected. THF, benzene, and benzene-d_6 were purified by distillation from sodium diphenylketyl under argon atmosphere. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded at 298 K on a Bruker DRX-500 spectrometer using residual non-deuterated solvents as internal reference. TrmSH (**2**) was prepared according to our method (*17*).

Table 1. Selected bond lengths (Å) and angles (deg) for **3**.

Bond lengths			
C(1)–S(1)	1.854(3)	Li(1)–N(1)	2.032(7)
S(1)–Li(1)	2.338(7)	Li(2)–N(1)	1.990(7)
S(1)–Li(2)	2.357(7)	Li(1)–Li(2)	2.692(9)
Li(1)–O(1)	1.891(7)	N(1)–Si(1)	1.698(3)
Li(2)–O(2)	1.900(7)	N(1)–Si(2)	1.702(3)
Bond angles			
C(1)–S(1)–Li(1)	133.81(19)	O(1)–Li(1)–N(1)	139.8(4)
C(1)–S(1)–Li(2)	129.63(19)	O(2)–Li(2)–N(1)	133.1(4)
Li(1)–S(1)–Li(2)	70.0(2)	Li(1)–N(1)–Li(2)	84.0(3)
S(1)–Li(1)–O(1)	122.1(3)	Li(1)–N(1)–Si(1)	107.5(2)
S(1)–Li(2)–O(2)	128.2(3)	Li(1)–N(1)–Si(2)	108.8(3)
S(1)–Li(1)–N(1)	97.8(3)	Li(2)–N(1)–Si(1)	115.9(3)
S(1)–Li(2)–N(1)	98.4(3)	Li(2)–N(1)–Si(2)	104.6(2)

4.1. *Synthesis of the mixed aggregate (3)*

A hexane solution of n-BuLi (1.57 M, 0.040 mL, 0.063 mmol) at room temperature was added to a benzene solution (2.5 mL) of thiol **2** (50.0 mg, 0.055 mmol). After stirring for 1 h, a THF solution of $(Me_3Si)_2NLi$ (0.42 M, 0.60 mL, 0.25 mmol) was added and the mixture was further stirred at room temperature for 30 min. The solvent was removed under reduced pressure, and the residue was recrystallized from benzene/THF to afford **3** (37 mg, 0.031 mmol, 56%) as colorless crystals. **3**: Colorless crystals; mp 265.6–267.2°C (decomp). ^{1}H NMR (C_6D_6, 500 MHz): δ 0.17 (s, 18H), 1.23 (broad multiplet, 8H), 2.03 (broad singlet, 36H), 3.57 (broad multiplet, 8H), 6.52 (broad triplet, 3H), 7.03-7.13 (m, 18H), 7.53 (broad doublet, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz): δ 2.35, 21.14, 62.39, 126.55, 126.85, 128.05, 128.34, 128.76, 140.00, 141.60, 142.36 (the carbon signals for coordinated THF molecules were not identified due to considerable broadening).

4.2. *X-ray crystallography*

Single crystals of **3** were grown in their benzene/THF solutions. The intensity data were collected at 120 K on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71069$ Å). The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97 (*25*). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were idealized by using the riding models. Crystallographic data for **3**: $C_{81}H_{97}Li_2NO_2SSi_2$, $M = 1218.76$, monoclinic, space group $P2_1/c, a = 16.636(6),\ b = 16.938(7),\ c = 25.950(11)$ Å, $\beta = 97.665(6)°,\ V = 7246(5)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.117\ \text{g cm}^{-3}$, 46361 measured reflections, 12669 independent, 820 parameters. $R_1 = 0.0933(I > 2\sigma(I))$, w$R_2 = 0.1834$ (all data). Goodness-of-fit on $F^2 = 1.167$. Crystallographic data for the structure of **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 721294.

Acknowledgements

This work was partly supported by Grants-in-Aid for Scientific Research (K.G. and T.K.) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also thank Tosoh Finechem Corporation and Shin-Etsu Chemical Co., Ltd. for the generous gifts of alkyllithiums and silicon compounds, respectively.

References

(1) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1624–1654.

(2) Jackman, L.M.; Rakiewicz, E.F. *J. Am. Chem. Soc.* **1991,** *113,* 1202–1210.

(3) Kremer, T.; Harder, S.; Junge, M.; Schleyer, P.v.R. *Organometallics* **1996,** *15,* 585–595.

(4) Jacobson, M.A.; Keresztes, I.; Williard, P.G. *J. Am. Chem. Soc.* **2005,** *127,* 4965–4975.

(5) Pauer, F.; Power, P.P. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P.v.R., Eds.; Wiley: New York, 1995, pp 295–392.

(6) Janssen, M.D.; Grove, D.M.; van Koten, G. *Prog. Inorg. Chem.* **1997**, *46,* 97–149.

(7) Englich, U.; Ruhlandt-Senge, K. *Coord. Chem. Rev.* **2000,** *210,* 135–179.

(8) Aslam, M.; Bartlett, R.A.; Block, E.; Olmstead, M.M.; Power, P.P.; Sigel, G.E. *J. Chem. Soc., Chem. Commun.* **1985,** 1674–1675.

(9) Ellison, J.J.; Power, P.P. *Inorg. Chem.* **1994,** *33,* 4231–4234.

(10) Ruhlandt-Senge, K.; Englich, U.; Senge, M.O.; Chadwick, S. *Inorg. Chem.* **1996,** *35,* 5820–5827.

(11) Niemeyer, M.; Power, P.P. *Inorg. Chem.* **1996,** *35,* 7264–7272.

(12) Janssen, M.D.; Rijnberg, E.; de Wolf, C.A.; Hogerheide, M.P.; Kruis, D.; Kooijman, H.; Spek, A.L.; Grove, D.M.; van Koten, G. *Inorg. Chem.* **1996,** *35,* 6735–6741.

(13) Veith, M.; Koban, A.; Huch, V. *Helv. Chim. Acta* **1998,** *81,* 1640–1644.

(14) Blair, S.; Izod, K.; Harrington, R.W.; Clegg, W. *Organometallics* **2003,** *22,* 302–308.

(15) Hildebrand, A.; Lönnecke, P.; Silaghi-Dumitrescu, L.; Silaghi-Dumitrescu, I.; Hey-Hawkins, E. *Dalton Trans.* **2006,** 967–974.

(16) Goto, K.; Holler, M.; Okazaki, R. *J. Am. Chem. Soc.* **1997,** *119,* 1460–1461.

(17) Goto, K; Hino, Y.; Kawashima, T.; Kaminaga, M.; Yano, E.; Yamamoto, G.; Takagi, N.; Nagase, S. *Tetrahedron Lett.* **2000,** *41,* 8479-8483.

(18) Shimada, K.; Goto, K.; Kawashima, T.; Takagi, N.; Choe, Y.-K.; Nagase, S. *J. Am. Chem. Soc.* **2004,** *126,* 13238–13239.

(19) Goto, K.; Kawashima, T. *J. Synth. Org. Chem., Jpn.* **2005,** *63,* 1157–1170.

(20) Goto, K.; Shimada, K.; Furukawa, S.; Miyasaka, S.; Takahashi, Y.; Kawashima, T. *Chem. Lett.* **2006,** *35,* 862–863.

(21) Chivers, T.; Krahn, M.; Parvez, M.; Schatte, G. *Chem. Commun.* **2001,** 1922–1923.

(22) Walfort, B.; Lameyer, L.; Weiss, W.; Herbst-Irmer, R.; Bertermann, R.; Rocha, J.; Stalke, D. *Chem.-Eur. J.* **2001,** *7,* 1417–1423.

(23) Engelhardt, L.M.; Jolly, B.S.; Junk, P.C.; Raston, C.L.; Skelton, B.W.; White, A.H. *Austr. J. Chem.* **1986,** *39,* 1337–1345.

(24) Mack, H.; Frenzen, G.; Bendikov, M.; Eisen, M.S. *J. Organomet. Chem.* **1997,** *549,* 39–43.

(25) Sheldrick, G.M. *SHELXL-97. Computer Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.