5376 *Inorg. Chem.* **1994,** *33,* 5376–5377

Synthesis and Characterization of $[Zn(SEt)Et]_{10}$, Formed via Insertion of Sulfur into Zn–C Bonds: A New Class of Wurtzite-like Cluster Framework

Dongshui Zeng, Mark J. Hampden-Smith,* and Eileen N. Duesler

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Received June 14, 1994

Metal thiolate compounds exhibit a rich and interesting structural chemistry that has been studied extensively.[1-6] These complexes are of scientific and technological interest as a result of their structural similarity to metalloproteins and metallothioneins[7] and the possibility that they can be used as precursors for the formation of binary metal sulfides.[8-11] Furthermore, as a result of the tendency of these species to oligomerize,[3-6,12,13] recent interest has focused on the formation of large molecular aggregates, often containing sulfide ligands, S^{2-},[14-23] which exhibit interesting optical and electronic properties.[24] Large Zn and Cd alkanethiolate and sulfide clusters are of particular interest because they generally exhibit a core structure that is analogous to that of the bulk, sphalerite-phase metal sulfide.[3] As a result, they can be used to test structural theories because these species should exhibit properties that are intermediate between those of nanometer-sized MS particles[25] and those of discrete molecular species.[24] In this paper we describe the synthesis, characterization and thermal decomposition of a new molecular zinc thiolate cluster, $Zn_{10}(SEt)_{10}Et_{10}$, formed via the insertion of S into half the M–C bonds of $ZnEt_2$. In contrast to other examples of Zn and Cd alkanethiolate clusters, this species exhibits a new molecular structural architecture, more closely related to wurtzite than to sphalerite-phase ZnS. However, it should be noted that the cluster reported here as well as other Zn–S clusters share the coordination principle of edge-shared MS_4 tetrahedra.

The reaction of a toluene solution of $ZnEt_2$ with 1 equiv of sulfur ($^1/_8S_8$) results in dissolution of the sulfur to form a colorless solution (see supplementary material for synthesis and characterization data). After addition of *n*-pentane and cooling, colorless crystals were isolated that have the empirical formula [Zn(SEt)Et], as determined by elemental analysis. The ^1H and ^{13}C NMR spectroscopy were also consistent with this empirical formula, showing the presence of a large number of different types of overlapping Zn–Et and Zn–SEt resonances which could not be distinguished even at high fields. The insertion of S into M–C bonds has recently been reported for the case of Grignard-type reagents, but has not been extensively studied for other M–C bonds.[1] The reaction of S_8 with transition metal complexes generally leads to the formation of metallapolysulfane complexes containing polysulfide $(S_x)^{2-}$ chains.[8,26-28] Characterization of the crystals isolated from this reaction by single-crystal X-ray diffraction revealed the molecular formula, $Zn_{10}(SEt)_{10}Et_{10}$. The structure of this molecule is shown in Figure 1a and consists of three six-membered, chair conformation Zn–S rings each linked together through three Zn–S bonds with capping SEt and Zn–Et groups at each end respectively.[38] This structural unit bears a striking resemblance to the wurtzite structure of bulk crystalline ZnS, as shown by comparison to the $[ZnS]_9$ wurtzite fragment drawn in Figure 1b.[29,30] To our knowledge, this is the first example of the observation of a wurtzite-like core structure in a zinc or cadmium thiolate cluster. Unfortunately, the quality of the structural data does not warrant a detailed discussion of the metrical parameters of this molecule, but the Zn–S and Zn–C bond lengths are in the normal range (see supplementary material). Numerous attempts to obtain better crystals and better quality crystallographic data at low temperatures did not result in better quality data than that reported here.

Other examples of compounds with empirical formula $[Zn(SR)R']_n$ have been prepared by the reaction of ZnR'_2 with 1 equiv of HSR.[31] The species that have been structurally characterized, $[MeZn(S\text{-}t\text{-}Bu)]_5$[32] and $[MeZn(S\text{-}i\text{-}Pr)]_8$,[33] do not resemble either sphalerite or wurtzite structures. However, it is interesting to note that the species found in the solid state to be $[MeZn(S\text{-}i\text{-}Pr)]_8$[33] is hexameric in benzene solution. At this

---

* Author to whom correspondence should be addressed.

(1) Bonasia, P. J.; Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 6777.

(2) *Journal of Electronic Materials: Special Issue on Wide-Bandgap II-IV Semiconductor Materials*; TMS: New York, 1993; Vol. 22, pp 429–577.

(3) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

(4) Dance, I. G.; Garbutt, R. G.; Craig, D. C.; Scudder, M. L.; Bailey, T. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1164.

(5) Dance, I. G.; Garbutt, R. G.; Bailey, T. D. *Inorg. Chem.* **1990**, *29*, 603.

(6) Dance, I. G.; Garbutt, R. G.; Scudder, M. L. *Inorg. Chem.* **1990**, *29*, 1571.

(7) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 769.

(8) Muller, A.; Diemann, E. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987; Vol. 2, Chapter 16.1.

(9) O'Brien, P. In *Inorganic Materials*; D. W. Bruce and D. O'Hare, Eds.; John Wiley & Sons Ltd.: 1992; pp 491.

(10) Osakada, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1117.

(11) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240.

(12) Craig, D.; Dance, I. G.; Garbutt, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 165.

(13) Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1983**, *22*, 1794.

(14) Lee, G. S. H.; Fisher, K. J.; Vassallo, A. M.; Hanna, J. V.; Dance, I. G. *Inorg. Chem.* **1993**, *32*, 66.

(15) Lee, G. S. H.; Fisher, K. J.; Craig, D. C.; Scudder, M. L.; Dance, I. G. *J. Am. Chem. Soc.* **1990**, *112*, 6435.

(16) Lee, G. S. H.; Craig, D. C.; Ma, I.; Scudder, M. L.; Bailey, T. D.; Dance, I. G. *J. Am. Chem. Soc.* **1988**, *110*, 4863.

(17) Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* **1990**, *112*, 1322.

(18) Herron, N.; Suna, A.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 2329.

(19) Herron, N.; Calabrese, J. G.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426.

(20) Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6825.

(21) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.

(22) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403.

(23) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141.

(24) Yang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525.

(25) Chandler, R. R.; Bigham, S. R.; Coffer, J. L. *J. Chem. Educ.*, in press.

(26) Muller, A.; Diemann, E. *Adv. Inorg. Chem. Radiochem.* **1987**, *31*, 89.

(27) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

(28) Banda, R. M. H.; Dance, I. G.; Bailey, T. D.; Craig, D. C.; Scudder, M. L. *Inorg. Chem.* **1989**, *28*, 1862.

(29) Sharma, R. C.; Chang, Y. A. In *Binary Alloy Phase Diagrams*, 2nd ed.; Scott, W. W., Ed.; 1990; Vol. 3, p 3297.

(30) Evans, H. T.; McKnight, E. T. *Am. Mineral.* **1959**, *44*, 1210.

(31) Bell, N. A.; Moseley, P. T. *J. Organomet. Chem.* **1987**, *325*, 47.

(32) Adamson, G. W.; Bell, N. A.; Shearer, H. M. M. *Acta Crystallogr.* **1982**, *B38*, 462.

(33) Adamson, G. W.; Shearer, H. M. M. *Chem. Commun.* **1969**, *16*, 897.

0020-1669/94/1333-5376$04.50/0

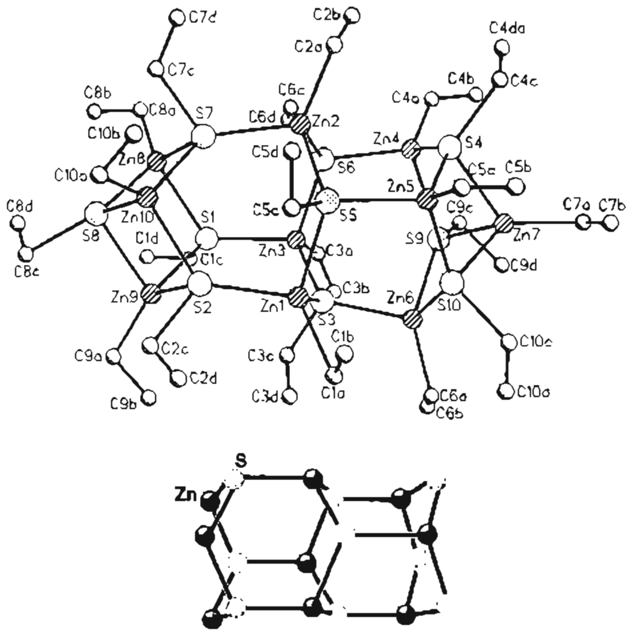

Figure 1. (a) Ball and stick drawing of the molecular structure of $Zn_{10}(SEt)_{10}Et_{10}$ emphasizing the geometry of the $[ZnS]_9$ core. (b) Portion of the structure of wurtzite ZnS.[30]

stage, it is not clear whether the molecular integrity of $Zn_{10}(SEt)_{10}Et_{10}$ is retained in solution, although the complexity of the ^1H and ^{13}C NMR data is consistent with the presence of this molecule.

As a result of the unusual wurtzite-like core structure of $Zn_{10}(SEt)_{10}Et_{10}$ and the fact that wurtzite-type ZnS is the high temperature (> 1000 °C) thermodynamically stable crystalline phase of ZnS,[29] we examined the thermal decomposition behavior of this molecular aggregate. However, it was anticipated that if the normal metal thiolate thermal decomposition pathway was followed, which involves elimination of alkyl sulfides (see eq 1), then a sulfur-deficient product should be

$$[M(SR)_2]_n \rightarrow nMS + nSR_2 \qquad (1)$$

formed. The compound $Zn_{10}(SEt)_{10}Et_{10}$ was heated under inert atmosphere to 250, 350, 450, and 700 °C for 30 min in separate experiments. Thermogravimetric analysis data revealed a slightly larger weight loss (39%) than expected (37%) for the formation of ZnS. X-ray diffraction data showed the presence of crystalline material with broad peaks corresponding to ~2 nm sized crystallites on heating to only 250 °C.[34] At higher temperatures, the peaks were sharper and corresponded to cubic (sphalerite) ZnS (see Figure 2) analogous to the results observed previously for the reaction between H_2S and $[EtZnS\text{-}t\text{-}Bu)]_5$.[35] TEM data gave analogous results. Analysis of the volatile byproducts formed on thermal decomposition at 350 °C showed the presence of C_2H_4, C_2H_6, $CH_3C(H)S$, and Et_2S, providing evidence for elimination of some sulfur-containing products. These results provide evidence that the structure of the molecular precursor *does not* direct the crystallization of a particular polymorph on solid-state thermolysis in this system. This observation is in contrast to the GaS[36] and InS[37] systems where the structure of the metastable phases formed by chemical vapor deposition (CVD) were related to the structural framework of the precursor, although the role of substrate in directing the crystallization process is not clear.

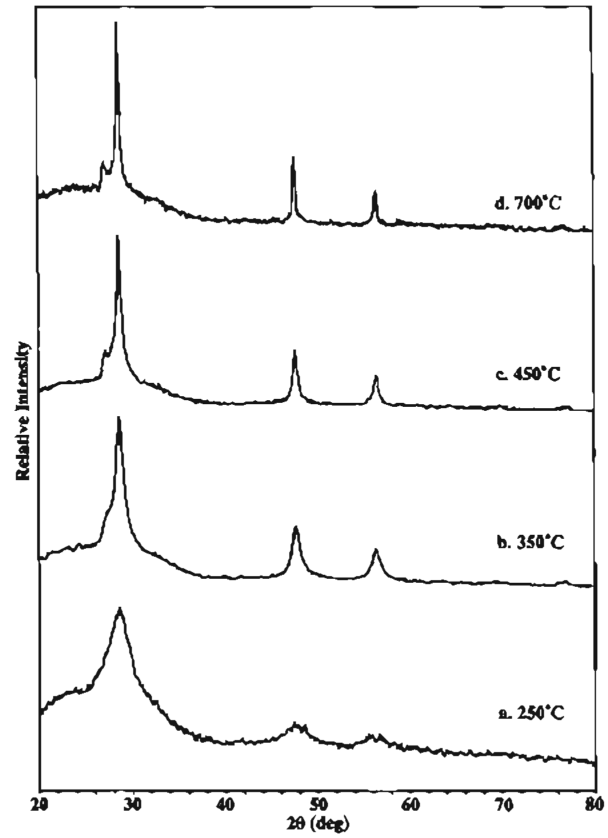

Figure 2. X-ray powder diffraction data for the solid obtained by thermal decomposition of $Zn_{10}(SEt)_{10}Et_{10}$ at 250−700 °C.

Acknowledgment. This work was funded by the Chemistry Division of the Office of Naval Research. M.J.H.S. thanks the Camile and Henry Dreyfus Foundation for a Teacher Scholar Award. We thank the NSF instrumentation program for the purchase of a low field NMR spectrometer, Prof. Ulrich Schubert for helpful discussions and Prof. Malcolm Chisholm and Dr. Bob Addleman, Indiana University, for the use of a 500 MHz NMR spectrometer. We thank Dr. Lu-Min Wang for assistance in obtaining TEM data on a JEOL 2000-FX instrument and the Department of Earth and Planetary Sciences for access to the X-ray diffraction facilities.

Supplementary Material Available: Text giving synthesis and characterization data for $Zn_{10}(SEt)_{10}Et_{10}$, tables of X-ray crystallographic data for $Zn_{10}(SEt)_{10}Et_{10}$, structure determination summary, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, H-atom coordinates, isotropic displacement coefficients, and text giving a refinement summary (20 pages). Ordering information is given on any current masthead page.

---

(34) Cullity, B. D. *Elements of X-ray Diffraction*, 2nd ed.; Addison-Wesley: Reading, MA, 1987.

(35) Guiton, T. A.; Czekaj, C. L.; Rau, M. S.; Geoffroy, G. L.; Pantano, C. G. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 503.

(36) MacInnes, A. N.; Power, M. B.; Barron, A. R. *Chem. Mater.* **1993**, *5*, 1344.

(37) MacInnes, A. N.; Cleaver, W. M.; Barron, A. R.; Power, M. B.; Hepp, A. F. *Adv. Mater. Opt. Electron.* **1992**, *1*, 229.

(38) Crystallographic data (Siemens R3m/V, graphite monochromator) for $Zn_{10}(SEt)_{10}Et_{10}$ at 293 K: space group $P\bar{1}$, $a = 12.010(2)$ Å, $b = 14.739(3)$ Å, $c = 20.327(4)$ Å, $\alpha = 99.93(3)°$, $\beta = 91.62(3)°$, $\gamma = 107.79(3)°$, crystal size (mm) = 0.299 × 0.460 × 0.690; octants collected = $-11 \leq h \geq 11$, $-13 \leq k \geq 13$, $-19 \leq l \geq 19$; $V = 3362.2\ (11)$ Å^3, $Z = 2$, d(calc) = 1.636 g/cm^3, $\lambda = 0.71073$, total reflections collected = 12 538, independent reflections = 6270, 2θ range = 3.0−60.0°, $R = 9.41\%$, $R_w = 9.00\%$. Data was collected from three different samples of crystals obtained from three independent reactions and grown from various solvents and also at low temperature (258 K). Although the refinement value is poor due to deterioration of the sample during data collection, this is the best data set available. The low temperature data set did not provide better data. See the supplementary material for details.