

Solution of a New Molecular Structure $\{[\text{SnClGe}(\text{SiC}_3\text{H}_9)_3]_4\}$ by Simulated Annealing

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Abstract

A crystal is known to possibly contain Sn, Ge, Si, C, Cl and H but the precise stoichiometry is unknown. In addition, the crystal seems to be highly disordered. The X-ray data did not yield to conventional direct methods. The structure has been solved by employing simulated annealing. The methodology involved is presented.

1. Introduction

Conventional direct methods have been known to be very effective in solving the structure of typical small molecules. However, they do not seem to work for macromolecules. This motivated us to seek an alternative method for solving the phase problem. We have demonstrated in previous publications (Su, 1995a,b) that simulated annealing (Kirkpatrick, Gelatt & Vecchi, 1983) offers a promising alternative. We have tested the method on several structures solved by direct methods and it yields essentially identical results. In this paper, we report a structure that seems to defy solution with direct methods. The structure has been solved by simulated annealing. Below, we first present the crystal data. The methodology is then discussed, followed by a description of the structure and a summary.

2. Crystal data

The crystal was synthesized by Geanangel *et al.* Blood red crystals of the cyclotetrahastannane product were prepared in a reaction of SnCl_2 with two equivalents of $\text{Li}(\text{THF})_{2.5}\text{Ge}(\text{SiMe}_3)_3$ in hexane. After workup, the product was crystallized from pentane at about 273 K over 30 d. Its red crystals were separated manually from colorless crystals of $[(\text{Me}_3\text{Si})_3\text{Ge}]_2\text{SnCl}_2$, which also formed in the reaction.

The space group is $F23$ (cubic) with unit-cell constant $a = 23.120 \text{ \AA}$. Neither the stoichiometry nor the Z number was known. The possible elements were Sn, Ge, Cl, Si and C. X-ray data were taken by J. D. Korp. 1712 reflections were obtained, with a resolution up to 1.0 \AA . Application of conventional direct methods failed to yield any sensible structure.

3. Methodology

As explained in previous publications (Su, 1995a,b), simulated annealing can be used to extract the atomic coordinates directly from the intensities (Semenovskaya, Khachatryan & Khachatryan, 1985; Karle, 1991) by minimizing the discrepancy between the calculated and observed intensities modeled by the following cost function E :

$$E(\{\mathbf{r}_i\}, \lambda) = \sum_{\mathbf{k}} [\lambda |F(\mathbf{k})| - |F(\mathbf{k})|_{\text{obs}}]^2, \quad (1)$$

where the structure factor $F(\mathbf{k})$ is calculated from the atomic scattering factor $f_i(\mathbf{k})$ and atomic coordinates \mathbf{r}_i in the usual fashion:

$$F(\mathbf{k}) = \sum_i f_i(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_i), \quad (2)$$

the summation being over all N atoms in the unit cell. Like the particle coordinates \mathbf{r}_i , the scale factor λ is determined by the the minimization procedure.

The above cost function is appropriate for a typical case in which the chemical formulas and the Z number are known beforehand. Since that information was not available for the structure we sought to solve, we have employed Gaussian spheres with optimum size (again determined by the optimization procedure) instead of real atoms to generate the charge density. We use Monte Carlo simulation to generate configurations of the Gaussians that minimize the cost function E . To speed up the computer code, in this simulation we have taken the difference between the calculated and observed intensities rather than the difference between the moduli of the calculated and observed structure factors in (1).

It is instructive to examine the cost function evaluated at various annealing temperatures. In Fig. 1, we plot the cost E as a function of the annealing temperature T . A linear cooling schedule was adopted in the simulation, 20 Gaussians were considered. It is clear from the plot that there is an abrupt drop in the cost function below a critical temperature. This resembles the first-order phase transition occurring in the solidification of a common liquid. In our simulation, about 1000 sweeps (a single sweep means a complete round of updating all particle positions) were covered at each temperature to ensure

thermal equilibrium. This is especially important near the phase transition. If the system is cooled too rapidly, the phase transition could be missed, and the system would become a supercooled liquid or a glass and the density profile would not correspond to reality.

After the annealing procedure is satisfactorily performed, a certain reconstruction is necessary to arrive at a sensible molecular structure. What we did was to lump the Gaussians that cluster within a typical atomic distance into one single atom. The charge of a particular atom is simply proportional to the number of Gaussians contained in the cluster. To obtain an accurate atomic number, we took an average over several independent runs. In that way, we were able to fix the ratio of the atomic numbers accurately enough to pinpoint all the non-H atoms in the unit cell. The R factors of the optimal Gaussian configuration are typically about 0.1. After all of the atoms in the crystal were determined, we replaced the Gaussians with real atoms and included the Debye factors for further refinement.

4. Molecular structures

It turns out that two distinct types of molecule co-crystallize in the unit cell. The smaller one, $\text{Ge}[\text{Si}(\text{CH}_3)_3]_4$, is too close to the reactant species to be of interest. So we will focus our attention on the other molecule. This molecule contains a cluster of Sn atoms at its core. A view of such a tin cluster along one of the threefold axes of its unit cell is shown in Fig. 2. A

novel feature of the cluster is that each Sn atom seems to split into three identical parts each carrying $1/3$ of the total charge. If one were to lump these three parts into a single Sn atom, one arrives at a tetrahedral tin skeleton. There are, however, two problems associated with this structure. First, the Cl atoms, which are adjacent to the cluster, are not accounted for in terms of bonding. Second, the three fragments of each Sn atom are too far apart to be lumped into a single atom. To solve the above problems, we assume that there are actually three distinct packing orientations of the molecule in each unit cell. X-rays pick up only the average. This would account for the three possible positions for each Sn atom. To determine the structure of a single copy of the molecule, we connect only pairs of atoms whose bond lengths are consistent with the expected values. Applied to the tin cluster in Fig. 2, this rule yields three distinct subclusters, which are color coded. Each subcluster corresponds to one possible orientation consistent with our assumption above. The complete structure of a single copy of the molecule is shown in Fig. 3. The coordinates of the atoms are listed in Table 1.

It is interesting to note that the tin skeleton resembles a buckled rectangle rather than a distorted tetrahedron. Another amusing point is that, in each unit cell, the threefold symmetry of the $F23$ group is broken. The symmetry is restored only by averaging over all unit cells. It should be mentioned that a similar degeneracy in packing orientation has occurred in tin compounds previously synthesized in Geanangel's labs.

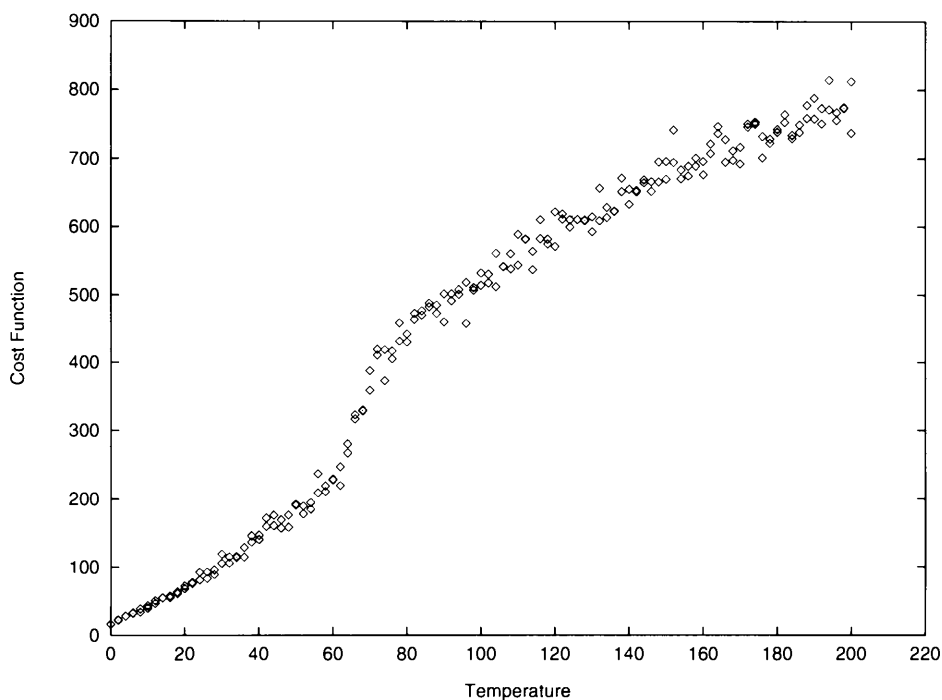


Fig. 1. Plot of the cost E as a function of the annealing temperature T . The scales are arbitrary.

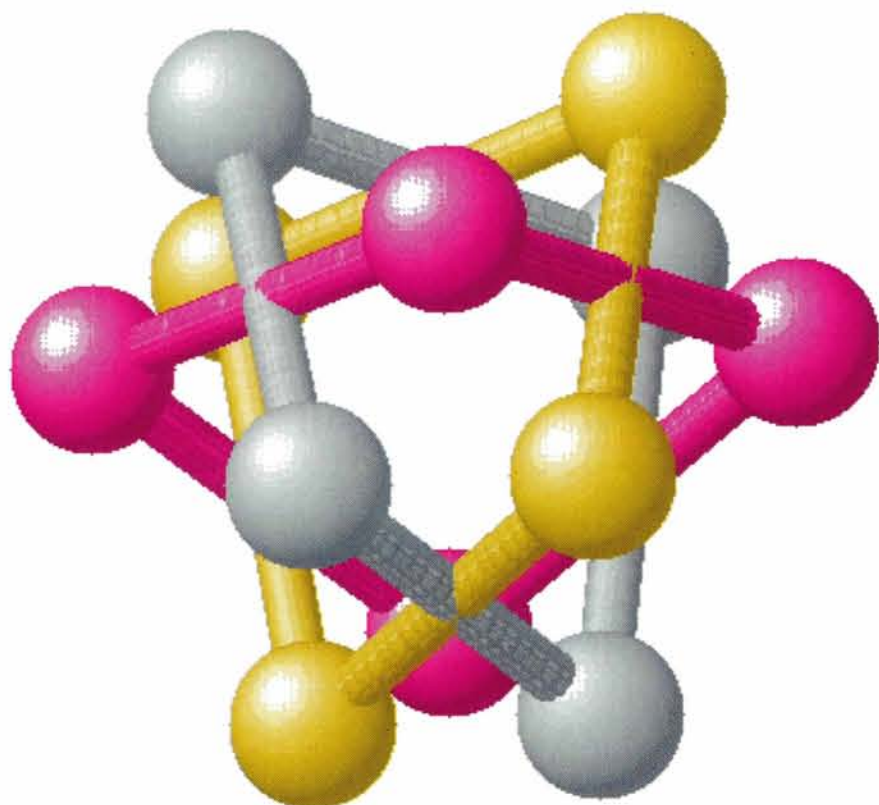


Fig. 2. Three distinct packing orientations of the tin core of the molecule $[\text{SnClGe}\{\text{Si}(\text{CH}_3)_3\}_3]_4$.

Table 1. *Fractional coordinates of the independent atoms in Fig. 3*

	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0.489	0.439	0.439
Cl	0.576	0.604	0.598
Ge	0.388	0.384	0.403
Si	0.310	0.446	0.358
C	0.258	0.393	0.333
C	0.278	0.490	0.420
C	0.337	0.493	0.292

There is also a twofold degeneracy for the smaller molecule. There are two distinct orientations opposite to each other. This molecule has a simple tetrahedral structure. It should be mentioned that our structure determination is supported by NMR data and a FABS mass spectrum. NMR (C_6D_6): ^1H , δ 0.560(*s*), 0.297(*s*); ^{13}C , δ 4.62, 3.43. The signals at δ 0.297 and 3.43 represented $\text{Ge}(\text{SiMe}_3)_4$, a byproduct that co-crystallized with the red product. A FABS mass spectrum using nitrophenyloctyl ether as a matrix did not give a parent

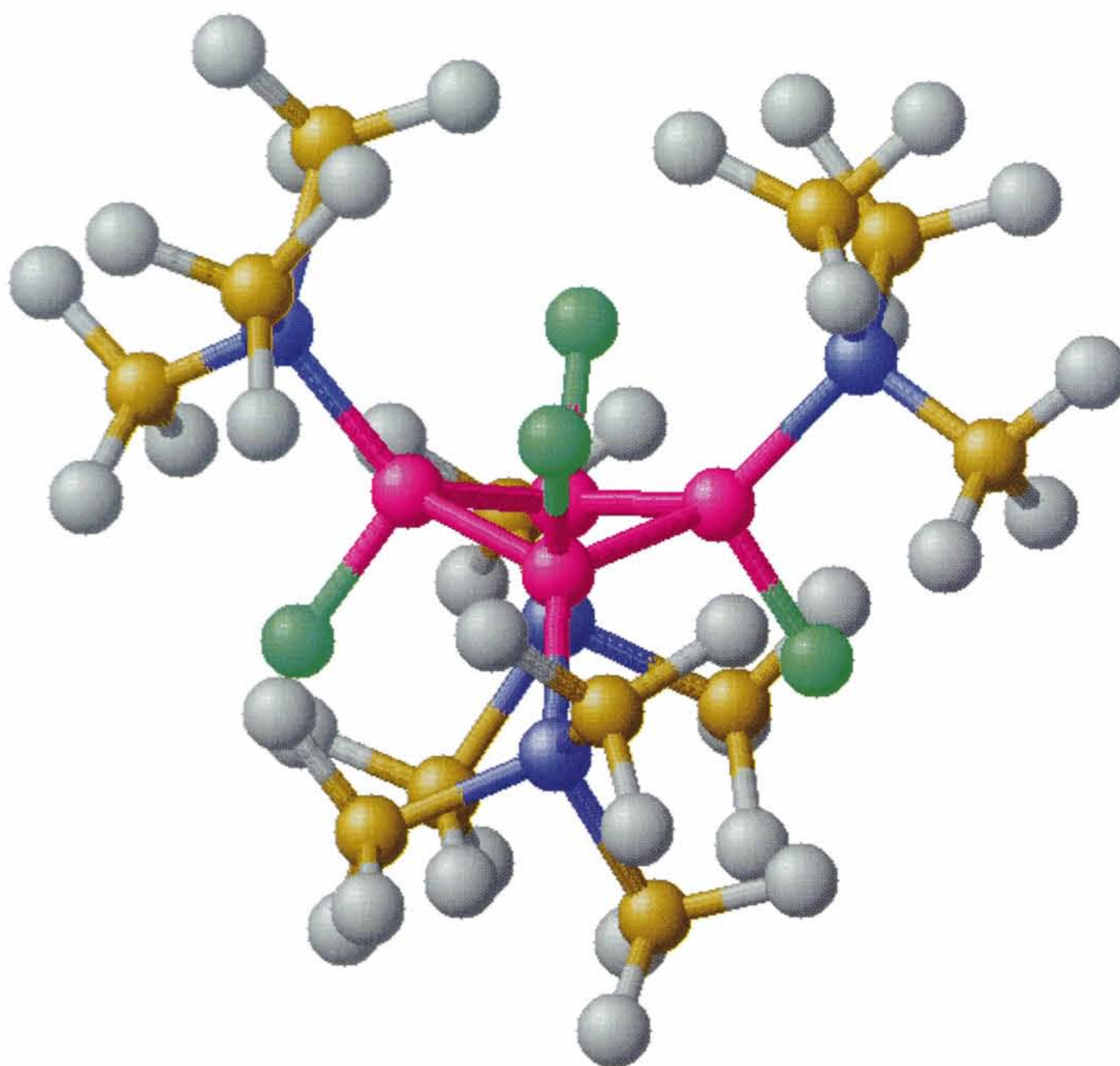


Fig. 3. Structure of $[\text{SnClGe}\{\text{Si}(\text{CH}_3)_3\}_3]_4$. Pink, blue, green, brown and gray correspond to Sn, Ge, Cl, Si and C, respectively.

envelope for $[\text{Sn}_4\text{Cl}_4(\text{GeR}_3)_4]$ ($R = \text{SiMe}_3$) but did not contain signals for several Sn_4 , Sn_3 and Sn_2 fragments, confirming the identity of the product as the proposed tetrastannane. The parent ion envelope for $[\text{Ge}(\text{SiMe}_3)_4]$ was also present.

5. Summary and future work

We have used simulated annealing to solve several crystal structures. In this paper, we report a structure which does not seem to be solvable by conventional direct methods. The flexibility and power of the simulated-annealing approach, as exemplified in this paper, may enable the method to deal with other difficult structures and macromolecules.

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References

- Karle, J. (1991). *Proc. Natl Acad. Sci. USA*, **88**, 10099–10103.
Kirkpatrick, S., Gelatt, C. D. Jr & Vecchi, M. P. (1983). *Science*, **220**, 671–680.
Semenovskaya, S. V., Khachatryan, K. A. & Khachatryan, A. G. (1985). *Acta Cryst.* **A41**, 268–273.
Su, W. P. (1995a). *Acta Cryst.* **A51**, 845–849.
Su, W. P. (1995b). *Physica (The Hague)*, **A221**, 193–201.