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An Extraordinarily Distorted *cyclo*-Tetrastibine. Crystallographic Structure of a New Polymorph of *cyclo*-(σ-C_5Me_5Sb)$_4$

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*Summary: A new crystalline polymorph of cyclo-(Cp*Sb)$_4$ has been crystallographically characterized that contains the mostly acutely angled four-membered, homoatomic ring system known (Sb−Sb−Sb = 76.1(1)°). In the previously reported form, the Cp* and Sb$_4$ ring centroids (viewed along the C−Sb bond) are anti; in the new form the Cp* ring rotates over 100° to a more crowded gauche form. The new form melts at a temperature 72 °C higher than the one previously reported and is about 15% more dense. While the Sb−Sb ring distances are normal (2.836(1) Å), the transannular Sb···Sb distances are the shortest known for antimony (3.518(1) Å) and apparently provide a stabilization that compensates for the extreme ring distortion.*

Introduction

We have sought new ways of incorporating antimony in hybrid transition-metal/main-group clusters.[1] Because homocyclic organoarsenic reagents had proved to be a very versatile class of reagents for the introduction into clusters of variously sized rings and chains of both substituted and naked arsenic atoms,[2] we believed that a potentially very attractive synthon would be *cyclo*-(σ-Cp*Sb)$_4$ (**1**; Cp* = C_5Me_5), reported by Lorberth, Müller, et al. in 1988.[3] However, either the products we obtained from reactions with a range of organometallic compounds were more easily prepared by other routes or yields were low. Additionally, these reactions were also often accompanied by the formation of Sb mirrors. Examples are given in eq 1 and 2. From an attempted

$$Mo(CO)_6 \xrightarrow[\text{24 h, 150 °C, toluene}]{cyclo\text{-}(Cp^*Sb)_4} [Cp^*Mo(CO)_3]_2 \qquad (1)$$

$$[CpMo(CO)_3]_2 \xrightarrow[\text{5 d, 125 °C, tolune}]{cyclo\text{-}(Cp^*Sb)_4} [CpMo(CO)_2]_2(\mu\text{-}\eta^2\text{-}Sb_2)^1 \qquad (2)$$

reaction of Cp_2NbH_3 with **1** (our goal was [$Cp_2Nb(H)$-(Cp*Sb=SbCp*)]), we recovered reddish orange crystals that proved to be a second polymorph of **1**. We now report the crystallographic structure of the new polymorph **1**-b, which possesses the most acutely angled four-membered homoatomic ring known and is considerably more dense than the polymorph previously reported (**1**-a).[3]

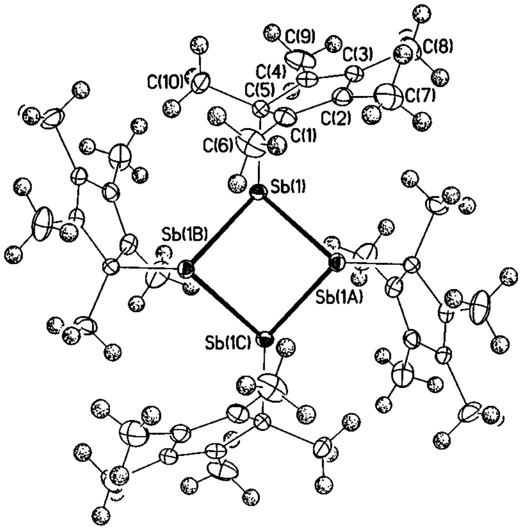

Figure 1. Top-down thermal ellipsoid (37% probability) diagram of polymorph **1**-b of *cyclo*-(Cp*Sb)$_4$ viewed along the tetragonal axis.

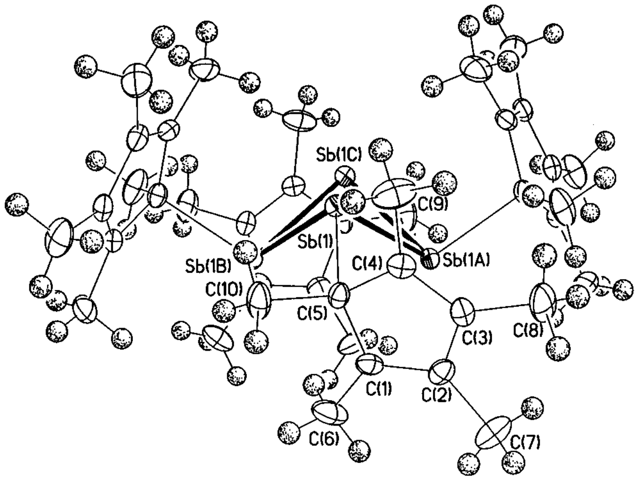

Figure 2. Side-on thermal ellipsoid (37% probability) diagram of polymorph **1**-b rotated ca. 90° from the view in Figure 1.

Polymorphism provides an opportunity to examine the extent to which bond parameters can be altered from normal ranges by intermolecular (packing) forces. Such knowledge of molecular solids is essential in differentiating between noteworthy intramolecular structural/chemical effects and the often less noteworthy expediencies of the crystal growth process.

Results and Discussion

A second polymorph of *cyclo*(Cp*Sb)$_4$ (**1**-b) was crystallized from a low-conversion reaction mixture contain-

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(1) Harper, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *390,* C36.

(2) DiMaio, A.-J.; Rheingold, A. L. *Chem. Rev.* **1990**, *90*, 169.

(3) (a) Berlitz, T. F.; Sinning, H.; Lorberth, J.; Müller, U. *Z. Naturforsch.* **1988**, *43B,* 744. (b) Lorberth, J.; Avtomonov, E. Private communication.

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Table 1. Comparisons of *cyclo*-(RSb)$_4$ Ring Systems[a]

R	Sb−Sb (Å)	Sb−Sb−Sb (deg)	fold angle (deg)	ref
tert-butyl	2.817(2) (1−2)	84.8(1) (1−2−3)	133 (1,2,3−1,4,3)	7
	2.814(2) (2−3)	85.2(1) (2−3−4)	133 (2,1,4−2,3,4)	
	2.817(2) (3−4)	84.9(1) (3−4−1)		
	2.821(2) (1−4)	85.1(1) (4−1−2)		
	2.817(1) (av)	85.0(1) (av)	133 (av)	
$(Me_3Si)_2CH$	2.866(1) (1−2)	80.75(1) (1−2−3)	115 (1,2,3−1,4,3)	8
	2.822(1) (2−3)	80.14(2) (2−3−4)	115 (2,1,4−2,3,4)	
	2.878(1) (3−4)	80.47(2) (3−4−1)		
	2.826(1) (1−4)	80.27(2) (4−1−2)		
	2.850(1) (av)	80.4(2) (av)	115 (av)	
Cp* (**1**-a)	2.856(1)	87.1(1)	144	3
Cp* (**1**-b)	2.836(1)	76.7(1)	104	this work
mesitylene[b]	2.855(1) (1−2)	76.91(2) (1−2−3)	120 (1,2,3−1,4,3)	9
	2.853(1) (2−3)	88.10(2) (2−3−4)	125 (2,1,4−2,3,4)	
	2.854(1) (3−4)	76.92(1) (3−4−1)		
	2.853(1) (1−4)	88.09(1) (4−1−2)		
	2.854(1) (av)	82.51(1) (av)	123 (av)	

[a] Additionally, a naked Sb_4^{2-} ring is known that is nearly flat and square and has an average Sb−Sb distance of 2.750(1) Å: Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1984**, *23*, 770. [b] The structure is solvated: *cyclo*-$(MesSb)_4 \cdot C_6H_6$.

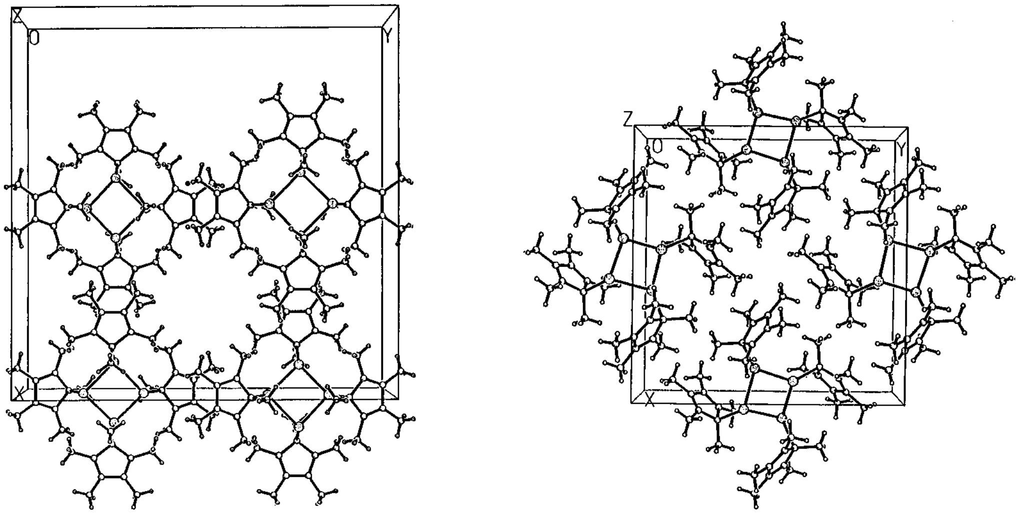

Figure 3. Comparison of unit-cell packing diagrams along the *z* axis for polymorphs **1**-a (left) and **1**-b (right).

ing Cp_2NbH_3 in toluene heated at 60 °C for 2 h. **1**-a is orange (mp 73 °C) and was recrystallized from hexane at −30 °C;[3b] **1**-b is reddish orange (mp 145 °C) and was recrystallized from warm benzene. In aliphatic and aromatic hydrocarbons and ethers, the forms are spectroscopically identical. Both polymorphs of *cyclo*-$(Cp^*Sb)_4$ crystallize in *I*-centered tetragonal cells as well-separated cyclotetrameric molecules. In both, crystallographic symmetry requires that all antimony atom environments be equivalent.[4] The structure of **1**-b is shown in Figures 1 and 2. Comparisons of **1**-b to **1**-a and to other four-membered cyclopolystibines are made in Table 1.

Perhaps the most striking difference between the two polymorphs is the efficiency of crystal packing (unit-cell diagrams for both are given in Figure 3). Lorberth, Müller, et al.[3] point out that their structure of **1**-a (D_{exptl} = 1.52 g cm^{-3} at −50 °C) contains a channel along the 4-fold axis large enough for a xenon atom to pass (4.84 Å diameter), while **1**-b has no significant void volumes and an extrapolated value for D_{exptl} at −50 °C of ca. 1.71 g cm^{-3}.[5]

Another conspicuous difference is the positions of the Cp* rings relative to the tetrastibine ring. For **1**-a, mirror-plane crystallographic symmetry imposes a 180° (*anti*) torsion angle for the construction formed by the Sb_4 ring centroid, an Sb atom, its attached carbon atom, and the Cp* centroid. For **1**-b, the same torsion angle is only 75.7°, requiring a rotation of over 100° around the Sb−C bond. Through this rotation, the bulky Cp* rings increase their separation but sharply decrease their separation from the Sb_4 ring. In compensation, the Sb−Sb−Sb angle contracts to a remarkably small 76.7(1)°, compared to 87.1(1)° in **1**-a, and slightly shortens the Sb−Sb distance to 2.836(1) Å, compared to 2.856(1) Å in **1**-a. Of the structures reported in the Cambridge Crystallographic Database,[6] **1**-b has the smallest ring angle of any homoatomic, four-membered system. In contrast, from the values for Sb−Sb bond distances in Table 1 and a more complete list in ref 7, the distances for **1**-a or **1**-b are within normal Sb−Sb single-bond ranges.

The bond parameter data in Table 1 show that the Sb_4 ring system has a considerable pliancy. The substituents in the five structurally characterized cyclotetrastibines are all bulky. Interestingly, their structures

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(4) **1**-a has $\bar{4}m2$ molecular symmetry, and **1**-b has $\bar{4}$ symmetry.

(5) We were unable to cool a crystal of **1**-b to −50 °C. The density at −50 °C is estimated from the observed thermal expansivity of similar materials.

(6) Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31.

Table 2. Crystallographic Data for *cyclo*-(Cp*Sb)$_4$ (1-b)

	(a) Crystal Data		
formula	$C_{40}H_{60}Sb_4$	V, Å^3	2073.5(9)
fw	1027.8	Z	2
cryst syst	tetragonal	D_{exptl}, g cm^{-3}	1.646
space group	$I\bar{4}$ (No. 84)	μ(Mo Kα), cm^{-1}	26.02
a, c, Å	15.895(3), 8.207(3)	T, K	294
	(b) Data Collection		
diffractometer	Siemens P3	no. of indep rflns	1712
2θ range, deg	4−60	no. of obsd rflns ($4\sigma F_o$)	1553
no. of rflns collected	1723	T_{max}/T_{min}	0.45/0.40
	(c) Refinement[a]		
$R(F)$, $R(wF)$	0.0204, 0.0271	data/param	15.2
$R(F)$, $R(wF)$ (all data)	0.0242, 0.0282	$\Delta\rho$, e Å^{-3} (max, min)	0.34, −0.36
GOF	1.01	Δ/σ (max, mean)	0.002, 0.000

[a] $R(F) = \sum\Delta/\sum(F_o)$; $R(wF) = \sum[\Delta w^{1/2}]/[F_o w^{1/2}]$; $\Delta = |F_o - F_c|$; $w^{-1} = \sigma^2(F_o) + gF_o{}^2$.

display several different schemes to reduce strain. When R = *t*-Bu, all of the Sb−Sb distances are short and identical, the 2.82 Å average being the shortest of the group, but the angles are normal (average 85.0°).[7] When R = $(Me_3Si)_2CH$, there is something of a long/short alternation in distances, but the average distance is normal and the angles fall in a narrow range.[8] The structure of *cyclo*-$(MesSb)_4{\cdot}C_6H_6$ contains a unique adaptation: there are rather short inter-ring Sb···Sb contacts (3.86 and 3.91 Å) between Sb_4 rings.[9] The two Sb atoms that participate in these close contacts have Sb−Sb−Sb angles (average 76.9°) similar to those found in **1**-b; the two isolated Sb atoms have considerably larger angles (average 88.1°) and overall have an average of 82.5°. In none of the other Sb_4-ring systems are there significant intermolecular contacts. In **1**-b, the shortest Sb···Sb contact is 7.28 Å (in **1**-a, 7.70 Å).

Ashe[10] has shown that several distibines ($R_2Sb{-}SbR_2$) crystallize in a fashion that aligns the Sb−Sb bonds end to end in an extended structure leading to intensely colored condensed phases. The intermolecular Sb···Sb distances are in the 3.6−3.7 Å range and are considerably shorter than the van der Waals radius separation (4.4 Å). Ashe[11] and others[12] have shown that there is likely extended bonding along the Sb−Sb···Sb−Sb chain. From this perspective, the intramolecular, transannular Sb···Sb contacts in **1**-b, 3.518(1) Å, are extraordinarily short; in fact, we are aware of none shorter.

Thus, it appears that the extraordinary differences between the two σ-Cp* polymorphs, which at first appear difficult to understand due to the extreme deformation of the Sb ring required to avoid contact with the *gauche* Cp* rings, may be explicable in terms of an increase in transannular stabilization achieved by decreasing the Sb−Sb−Sb angle. The modest color difference between the two forms (**1**-a, orange; **1**-b, red-orange) suggest that while the interaction is not particularly strong, it does occur twice. We would also suggest that the inefficient packing of the original polymorph may result from a solvent-guided crystal growth process in which the molecules of weakly bound hexane exit via the large channels as the crystals grow. Once the Cp* rings have begun to form interleaved layers, they are no longer able to rotate to form the higher melting, denser, and presumably more stable polymorph. No interleaving occurs in **1**-b.

Experimental Section

X-ray Structural Determination. Crystallographic data for **1**-b are summarized in Table 2. Our sample of **1** was obtained by a procedure adapted from the published procedure; SbF_3 was substituted for $SbCl_3$, and the product was recrystallized from warm benzene (mp 145 °C). A reddish orange specimen was affixed to a glass fiber with epoxy cement and found from photographic characterization to be tetragonal (Laue group $4/m$). Systematic absences in the reflection data were consistent with $I4$, $I\bar{4}$, or $I4/m$. E statistics strongly favored a noncentrosymmetric space group; with $Z = 2$ and a puckered ring, an initial choice of $\bar{4}$ molecular symmetry was made and was subsequently supported by the well-behaved refinement. A semiempirical correction for absorption based on ψ-scan data was applied to the data. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. An inspection of F_o vs F_c showed that a correction for secondary extinction was required (as described in the Supporting Information). The correctness of the reported enantiomer was determined by Rogers' test, which refines a multiplication term for $\Delta f''$ (η = 1.16(10)). All computations used SHELXTL (version 4.2) software (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Additional crystallographic data for **1**-b, including tables of atomic coordinates, bond parameters, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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[7] Mundt, O.; Becker, G.; Wessley, H.-J.; Breunig, H. J.; Kischkel, H. *Z. Anorg. Allg. Chem.* **1982**, *486*, 70.

[8] Ates, M.; Breunig, H. J.; Ebert, K.; Gülec, S.; Kaller, R.; Dräger, M. *Organometallics* **1992**, *11*, 145.

[9] Ates, M.; Breunig, H. J.; Gülec, S.; Offermann, W.; Häberle, K.; Dräger, M. *Chem. Ber.* **1989**, *122*, 473.

[10] Ashe, A. J., III; Ludwig, E. G., Jr.; Pommerening, H. *Organometallics* **1983**, *2*, 1573. Ashe, A. J., III; Diephouse, T. R.; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1991**, *10*, 2068.

[11] Ashe, A. J., III; Kausch, C. M.; Eisenstein, O. *Organometallics* **1987**, *6*, 1185.

[12] Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3876. Cowley, A. H. In *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; pp 75−80.