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The Molecular and Crystal Structures of (4-Halo-1,2,3,4-tetraphenyl-cis,cis-1,3-butadienyl)dimethylphenyltins

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The crystal structures of the (4-halo-1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyl)dimethylphenyltin compounds $(Sn(CH_8)_{2-})$ $(C_{6}H_{5})(C_{28}H_{20}X)$; X = Cl, Br) have been determined by three-dimensional X-ray diffraction methods. This study establishes the absence of $Sn \cdots X$ intramolecular bonding in these compounds and provides indirect support for the postulate that the rotational barriers observed in a series of dissymmetric butadienvitin halides are steric in origin. The title compounds, which are isomorphous, crystallize in the orthorhombic space group $Pna2_1$ with a = 15.643, b = 12.073, c = 15.527 Å for X = Cl and a = 15.890, b = 12.047, c = 15.563 Å for X = Br, all ± 0.010 Å at 25°. There are 4 molecules per unit cell. The intensity data were collected on a four-circle automatic diffractometer (Mo K α radiation) and the structures were solved by Patterson and Fourier methods. Refinement by full-matrix least squares gave conventional R factors of 6.2% for the 2847 reflections above background (chloro derivative) and 4.7% for 1724 reflections above background (bromo derivative). The dienes are skewed at angles of 92.9° (X = Cl) and 91.8° (X = Br) from the planar s-cis conformation. Intramolecular tinhalogen interactions appear to be weak, as indicated by the Sn $\cdot \cdot \cdot$ Cl (4.284 \pm 0.003 Å) and Sn $\cdot \cdot \cdot$ Br (4.346 \pm 0.002 Å) distances.

Introduction

The butadienvltin derivatives I-VI are of interest because they permit direct measurement of the ro-



tational barriers about the central bonds of 1,3-dienes *via* coalescence of the nmr signals of the diastereotopic methyl groups.^{1,2} However, the interpretation of these results for IV-VI was complicated by the discovery^{1,2} of a short⁸ intramolecular Sn \cdots Br distance of 3.774 \pm 0.005 Å in V, which raised the possibility that the observed barriers to exchange originated not only in steric hindrance to diene rotation but also in the breaking of a weak Sn...Br interaction where Br was acting as a Lewis base. Because tetraorganotin derivatives are believed not to coordinate with bases,⁴ I-III were synthesized to test this point. The virtual identity² of the corresponding barriers between I-III and IV–VI led us to conclude that rupture of $Sn \cdots X$ interactions were not in fact rate determining. The X-ray structural studies of I and II, reported below, were carried out to determine whether Sn ··· X interactions were indeed absent in the tetraorganotin series I-III and by inference to test the view¹ that the short $Sn \cdots Br$ distance in V (where steric factors are nearly equivalent) may represent a case of incipient pentacoordination at tin.

Experimental Section

Compounds I-III, prepared as described previously,1 crystallize as well-formed needles elongated on the c axis. Preliminary Weissenberg photographs indicated that I-III are isomorphous; the reciprocal lattice symmetry D_{2h} and the systematic absence of 0kl reflections for k + l odd and of h0l for h odd are consistent with space groups $Pna2_1$ (C_{22}) and Pnam (D_{2h}). Lattice constants and their errors (25°), which were established by leastsquares refinement of the setting angles of ten reflections on a Picker four-circle goniometer (Mo K α radiation, λ 0.71069 Å), are listed in Table I. Although these compounds can in prin-

	TABLE]	['	
	CRYSTAL DA	ATA ⁴	
	C36H31C1Sn	Ca6Ha1BrSn	C36H31ISn
Lattice	a 15.643 (7)	15.890(3)	16.295(2)
constants $\{l\}$	12.073 (4)	12.047(1)	12,156(2)
(25°), Å 🛛 🕻	: 15.527 (7)	15.563(3)	15.633(2)
Vol, Å ³	2932.4(1.0)	2979.2 (0.3)	3096.6(0.3)
Mol wt	617.75	662.21	709.20
Ζ	4	4	4
$\rho_{\rm ealed}$, g cm ⁻⁸	1.399	1.476	1.521
ρ _{obsd} , g cm ^{−3}	1.37(1)	1.46(1)	1.52(1)

^a The errors given in parentheses reflect the precision of the measurements as given by the least-squares program. All results are believed reproducible to 0.010 Å.

ciple adopt a geometry with C_s symmetry, the presence of two distinct methyl signals in the nmr spectrum¹ indicates that such a conformation does not occur in solution. Because the experimental densities (Table I), measured by flotation in aqueous NaI solutions, indicate 4 molecules per unit cell, the space group must be Pna21 if a molecular mirror plane is also absent, as expected, in the solid.

For the chloro derivative I, intensity data were gathered on a crystal of dimensions 0.29 \times 0.32 \times 0.64 mm mounted with its long (c) axis parallel to the ϕ axis of the diffractometer. The crystals are rectangular prisms, and the dimensions refer to the

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⁽¹⁾ F. P. Boer, G. A. Doorakian, H. H. Freedman, and S. V. McKinley, J. Amer. Chem. Soc., 92, 1225 (1970). (2) F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley, and V. R.

Sandel, ibid., 89, 5068 (1967).

⁽³⁾ The sum of van der Waals radii is taken to be 2.2 (Sn) + 1.95 (Br) = 4.15 Å.²

⁽⁴⁾ I. R. Beattie, Quart. Rev., Chem. Soc., 17, 382 (1963).

				IIOMIC I AKA	MEIEBS			
Atom	x/a	X = y/b	= C1	$B, Å^2$	x/a	X =	Br	$B, Å^2$
Sn	0.37720(3)	0.56621(4)	0.50079%		0.37975(6)	0.56477(7)	0.50079	
X	0.3855(1)	0.2163(2)	0.5462(2)		0.37865(10)	0.20847(12)	0,54416 (11)	
C(1)	0.3738(5)	0.4437(7)	0.4005(5)	3.03(15)	0.3765 (8)	0.4411 (10)	0,4007 (8)	3.01(23)
$\mathbf{C}(2)$	0.4283(5)	0.3599(7)	0.3932(6)	3.06(17)	0.4315(8)	0.3570(11)	0.3933 (8)	2.96 (28)
C(3)	0.4971(5)	0.3388(7)	0.4583(6)	2.73(14)	0.5001(7)	0.3374 (9)	0.4582(8)	2.12 (23)
C(4)	0.4858(5)	0.2700(7)	0.5253(5)	3.11(19)	0.4881(8)	0.2694(10)	0.5263(8)	3.26(30)
C(5)	0.4168(7)	0.5092 (9)	0.6279(7)	4,31 (20)	0.4175(9)	0.5096(12)	0,6290 (9)	4.07(32)
C(6)	0.2513(6)	0.6349(8)	0.6183(7)	5.42(28)	0.2548(8)	0.6328(11)	0.5184(11)	5.09 (35)
C(7)	0.3019(5)	0.4856(6)	0.3411 (6)	2.77(15)	0.3060 (8)	0.4569(10)	0.3418 (8)	3.04(28)
C(8)	0.2407(6)	0.3774(8)	0.3307(6)	3.79(21)	0.2439 (8)	0.3759(11)	0.3337 (9)	3.44(30)
C (9)	0.1749(6)	0.3928(9)	0.2699 (8)	4.58(24)	0.1785 (9)	0.3877(11)	0.2728(11)	4.11(34)
C(10)	0.1708(7)	0.4873(9)	0.2221(7)	4.70(22)	0.1723(9)	0.4855(13)	0.2265(10)	4.61(35)
C(11)	0.2311(7)	0.5673(9)	0.2310(7)	4.93(22)	0,2329(9)	0,5664(13)	0.2335 (9)	4.42(35)
C(12)	0.2961(6)	0.5549(8)	0.2917(7)	4.30(20)	0.2991(9)	0.5556(13)	0.2947(9)	4.33(32)
C(13)	0.4291(5)	0.2815(7)	0.3189(6)	2.87(18)	0.4320(8)	0.2816(11)	0.3187(8)	2.69(26)
C(14)	0.4210(6)	0.3188 (8)	0.2342(6)	3.84(21)	0.4200(8)	0.3183(11)	0.2346(9)	3.45(30)
C(15)	0.4185(7)	0.2420(9)	0.1650(7)	4.40(22)	0,4202(9)	0.2425(13)	0.1653(10)	4.36(35)
C(16)	0.4305(7)	0.1319(9)	0.1798(7)	4.71(23)	0.4316(10)	0.1323(13)	0.1793(10)	4 72 (36)
C(17)	0.4439(7)	0.0947(8)	0.2622(7)	4.68(23)	0.4469(9)	0.0930(12)	0.2606(11)	4.71 (35)
C(18)	0.4411(6)	0.1668(8)	0.3311(6)	3.60(18)	0.4473(8)	0.1664(11)	0.3304(9)	3.50(29)
C(19)	0.5808(5)	0.3935(7)	0.4425(6)	2.76(15)	0.5819(7)	0.3912(9)	0.4428(8)	2.33(24)
C (20)	0.6224(5)	0.4473(6)	0.5107(8)	4.10(19)	0.6228(8)	0.4453(10)	0.5133(9)	3.90 (27)
C(21)	0.7010(6)	0.4992(8)	0.4967 (10)	5.04 (20)	0.7029(8)	0.4986(12)	0.4973(12)	5.24 (32)
C(22)	0.7376 (8)	0.4963 (10)	0.4156(8)	5.65(26)	0.7386(10)	0.4959(14)	0.4179 (11)	5.67(40)
C(23)	0.6978(7)	0.4416(9)	0.3468(8)	5.11(24)	0.6991 (10)	0.4430(13)	0.3487(10)	4.85(34)
C(24)	0.6153(6)	0.3926 (8)	0.3627(7)	4.07(20)	0.6173(9)	0.3915(11)	0.3636 (9)	4.02 (31)
C(25)	0.5515(6)	0.2259(8)	0.5837(6)	3.38(19)	0.5530(8)	0.2263(12)	0.5844(9)	3.54 (31)
C(26)	0.5418(6)	0.2293(8)	0.6755(7)	3.82(19)	0.5422(8)	0.2310(11)	0.6755(9)	3.01(28)
C(27)	0.6081(6)	0.1890 (8)	0.7281(6)	3.81(19)	0.6067(9)	0.1899(11)	0.7287(10)	4.18 (33)
C(28)	0.6784(6)	0.1483(9)	0.6925(7)	4.11(23)	0.6780(9)	0.1470(12)	0.6923 (9)	3.77 (32)
C(29)	0.6917(7)	0.1439(9)	0.6028(8)	3.13(24)	0.6897(9)	0.1398(12)	0.6047(10)	4.60(35)
C(30)	0.6270(6)	0.1813(7)	0.5461(6)	3.92(18)	0.6260(8)	0.1784 (10)	0.5492(9)	3.58 (26)
C(31)	0.4536(5)	0.7012(7)	0.4604(6)	3.25(17)	0.4564(7)	0.7001 (10)	0.4581(9)	3.34(28)
C (32)	0.4306(6)	0.8073(8)	0.4875(7)	4.75(22)	0.4346(8)	0.8057 (11)	0.4853(9)	4.27(33)
C(33)	0.4814(7)	0.8984(9)	0.4617(8)	5.44(22)	0.4835(10)	0.8976(12)	0.4623(11)	5.23(40)
C(34)	0.5480(8)	0.8861 (10)	0.4099(8)	5.42(24)	0.5507(11)	0.8832 (14)	0.4095(11)	5.34(41)
C(35)	0.5692(7)	0.7817 (11)	0.3817(8)	5.91(30)	0.5725(11)	0.7767 (16)	0.3808(11)	5.90(43)
C(36)	0.5235(7)	0,6870(9)	0.4070(7)	4.94(25)	0.5267(10)	0.6843(13)	0.4055(10)	4.89(38)

TABLE II^a Atomic Parameters

Anisotropic Temperature Factors^c

	10 ⁵ β ₁₁	105 <i>β</i> 22	105333	$10^{5}\beta_{12}$	10 ⁵ <i>B</i> 13	10 ⁵ \$23
Sn (X = Cl)	356 (2)	612(4)	376(2)	-14(3)	-15(4)	-59(5)
C1	309(10)	906(21)	470 (12)	-86 (14)	68(10)	188(14)
Sn (X = Br)	364(4)	581(6)	391(4)	-5(6)	-28(8)	-39(6)
Br	345(6)	891(14)	506 (7)	-95(10)	59(9)	182(9)

^a Standard errors referred to the last significant digit are given in parentheses. ^b The z coordinate of the Sn atom is fixed as permitted. by the space group. ^c Anisotropic temperature factors are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$.

a, b, and c axes, respectively. The intensities of 3541 independent reflections were measured by the θ -2 θ scan technique with Mo K α radiation selected using the (002) reflection of a highly oriented graphite crystal monochromator. The X-ray tube was set at a 4° takeoff angle, and a detector aperture 6.0 mm square was positioned 30 cm from the crystal. Scan angles from 2.2 to 2.4° were employed over the range (0-0.461) of sin θ examined. Attenuators prevented the count rate from exceeding 12,000/sec. The scan speed was 2°/min. Background counts of 10 sec were taken at each end of the scan by the stationary-crystal, stationary-counter method. The (330) reflection was monitored every 50 measurements and showed a maximum deviation of $\pm 1\%$. An error $\sigma(I) = [(0.02I)^2 + N_0 +$ $k^2 N_{\rm b}$]^{1/2} was assigned to the net intensity $I = N_0 - k N_{\rm b}$ in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent leastsquares refinement. Here N_0 is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities corrected for Lorentz and polarization effects by the expression $Lp^{-1} = \sin 2\theta (1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta)$ $\cos^2 2\theta_m$) where $2\theta_m = 12.16^\circ$ is the monochromator setting angle. The 694 reflections for which either I < 0 or $\sigma(I)/I > 0.5$ were denoted absent and were not used in the structure analysis. The linear absorption coefficient for I is $\mu(Mo K\alpha) = 9.7 \text{ cm}^{-1}$. Transmission factors were estimated to vary by less than $\pm 2\%$ about a mean value, and, therefore, absorption corrections were considered unnecessary. Essentially the same experimental configuration was used to collect data from the bromo derivative II. However, due to the relatively weak scattering of II, not as many higher order reflections were observed. Data were collected from a crystal of hexagonal cross section, with a width varying between 0.17 and 0.20 mm and a length of 0.50 mm. A total of 2889 independent reflections was measured, covering the sphere $0 \le \sin \theta \le 0.42$. Of these 1163 were defined absent under somewhat more selective criteria $(I < 0 \text{ or } \sigma(I)/I > 0.3)$ than were used for I. Fluctuations in the test reflection (220) were all within $\pm 4\%$. A cylindrical absorption correction¹ was applied to the data using μ (Mo K α) = 21.8 cm⁻¹ and r = 0.0097cm. Transmission coefficients ranged between 0.70 and 0.75.



Figure 1.—Three-dimensional view of the molecular structure of (4-chloro-1,2,3,4-tetraphenylbutadienyl)dimethylphenyltin. The tin and chlorine atoms are represented by 50% probability thermal ellipsoids.

Solution and Refinement of the Structure

The tin and the halogen atoms were located in normal-sharpened Patterson functions.¹ Electron density maps⁵ based on the heavy-atom phases contain false mirror planes at z = 0 and $z = \frac{1}{2}$. Our initial attempts to resolve this ambiguity involved Fourier methods and tangent refinement of the heavy-atom phases,⁶ when two phenyl rings were correctly chosen from a Fourier, the rest of the structure became obvious.

Least-squares refinement^{7,8} of the atomic positions and isotropic temperature factors for the chloro derivative was initiated on a small computer using blocks of 72 variables and a truncated data set of 1907 reflections. $R_1 = \Sigma ||F_o| - |F_o||/\Sigma |F_o|$ was reduced from its initial value of 0.140 to 0.062, while $R_2 = \{ \Sigma w \cdot \}$ $(|F_{o}| - |F_{c}|)^{2}/\Sigma w F_{o}^{2}$ dropped from 0.163 to 0.059. Refinement was completed on a larger computer using full-matrix least squares⁹ on the entire observed data set of 2847 reflections, assuming anisotropic temperature factors for the Sn and Cl atoms. After three cycles R_1 converged from 0.071 to its final value of 0.060 and R_2 was reduced from 0.061 to 0.053. The average positional shift in the final cycle was 0.03σ with a maximum shift of 0.18σ . The final difference map gave no positive regions greater than $0.86 \text{ e}^{-/\text{Å}^3}$ or negative regions lower than $-1.1 \text{ e}^{-}/\text{Å}^{3}$. The hydrogen atoms were not located. The effects of secondary extinction appear to be negligible and no correction was made.

The structure of the bromo derivative was refined using the final positions determined for the chloro analog. The starting R factors for the 1726 observed reflections were $R_1 = 0.135$ and $R_2 = 0.142$. These dropped to 0.064 and 0.059, respectively, after three cycles of block isotropic refinement as described previously. Anisotropic temperature factors were again introduced for the tin and the halogen and after four cycles of full-matrix least squares R_1 and R_2 dropped to their final values of 0.047 and 0.045, respectively. The maximum parameter shift in the final cycle was 0.03σ ; the average shift was less than 0.01σ . For this structure the final difference map showed no negative density below $-0.74 \text{ e}^-/\text{Å}^3$ or positive peaks above $+0.61 \text{ e}^-/\text{Å}^3$.

The final atomic parameters and their estimated standard deviations are listed in Table II, while Tables IIIA and IIIB tabulate the observed and calculated structure factors. The root-mean-square amplitudes of vibration of the heavy atoms and their direction cosines are given in Table IV. Bond distances and angles are listed in Tables V and VI, respectively. The standard errors given in Tables IV-VI were calculated from the variance-covariance matrices obtained in the final least-squares cycles.¹⁰ The molecular structure of I is shown¹¹ in Figure 1 with tin and chlorine thermal parameters represented by thermal ellipsoids.

Discussion

This investigation confirms the absence of any appreciable $Sn \cdots X$ interactions in I and II. The $Sn \cdots CI$ (4.284 \pm 0.003 Å) and $Sn \cdots Br$ (4.346 \pm 0.002 Å) intramolecular distances exceed the respective sums of van der Waals radii³ (4.00 and 4.15 Å) and appear to be limited by contacts¹² with the organic ligands on tin. By contrast, the $Sn \cdots Br$ distance in V was 0.38 Å *less* than the sum of van der Waals radii and 0.57 Å less than this distance in II. These structural differences indicate that substitution of a halogen for one organic group on a tetraorganotin may increase the Lewis acidity sufficiently to permit an interaction with the vinylic halide.

⁽⁵⁾ J. Gvildys, "Two- and Three-Dimensional Crystallographic Fourier Summation Program," based on MIFRI, Program B-149, Program Library, Argonne National Laboratory, Argonne, Ill.

⁽⁶⁾ Using the tangent refinement program FAZE, by G. N. Reeke, J. Amer. Chem. Soc., 90, 1663 (1968).

⁽⁷⁾ XFLS, by F. P. Boer and F. P. van Remoortere, is a full-matrix crystallographic least-squares program for the IBM 1130 computer. Core and disk storage limitations restrict it to 72 simultaneously varied parameters and 2000 reflections. The function $\Sigma w(|F_0| - |F_0|)^2$ is minimized.

⁽⁸⁾ Atomic scattering factors were obtained from "The International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 201. No dispersion corrections were made.

⁽⁹⁾ J. Gvildys, ANLFLS-14E, a version of oRFLS by W. R. Busing, K. O. Martin, and H. A. Levy adapted for the CDC 3800 computer.

⁽¹⁰⁾ J. Gvildys, anlfff, a version of orfffe the fortran crystallographic function and error program by Busing, Martin, and Levy.

⁽¹¹⁾ C. Johnson, ORTEP, a FORTRAN thermal ellipsoid program, Oak Ridge National Laboratory, Oak Ridge, Tenn.

⁽¹²⁾ The CH₈(5) $\cdot \cdot \mathbf{X}$ distances are 3.78 Å for $\mathbf{X} = \text{Cl}$ and 3.91 Å for $\mathbf{X} = \text{Br}$, very close to the respective sums of van der Waals radii for a methyl and a halogen, 3.80 and 3.95 Å.

TABLE IIIA Observed and Calculated Structure Factors in Electrons for X = Cl

											T	BLE	z II	IA	(Con	ntin	ued	()	1. C													
K L FORS FCAL	ĸ	FORS FCA		FORS	FCAL	ĸu	FORS	FCAL	ĸι	F 085	FCAL	ĸ	FOBS I	FCAL	ĸ	FORS	FCAL	ĸ	FORS	FCAL	۴ ۱	FORS	FCAL	ĸ	FORS	FCAL	ĸι	FORS	FCAL	4 L	FUBS	FCAL
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Several other structural features are related to this result. For example, the amount of skew between the two ethylenic moieties is considerably higher in I and II than in the intramolecularly bonded dihalide V: the dihedral angle between the C(1)-C(2)-C(3) and the C(2)-C(3)-C(4) planes is $92.9 \pm 1.1^{\circ}$ for I and $91.8 \pm 1.6^{\circ}$ for II, vs. 68.1° in V,¹ with 0° defined as the planar s-cis conformation.

The structures of several highly skewed 1,3-dienes have now been reported;^{1,18-15} the present structure is an example where the π lobes of the double bonds are virtually at right angles and no conjugation can be expected. It is, therefore, interesting to note that our two independent values of the 2,3 single-bond length, 1.498 ± 0.011 Å (I) and 1.505 ± 0.016 Å (II), do not differ significantly from the value reported for the planar system in cis, cis-tetraphenylbutadiene, 16 1.493 Å. However, our values are about 0.04 Å longer than the value of 1.463 ± 0.003 Å in butadiene itself,¹⁷ which is also planar. This difference is approximately three standard deviations in each case. Our values also agree closely with C-C bonds of 1.508 ± 0.013 and 1.505 ± 0.010 Å in two other highly skewed tetraphenylbutadiene derivatives.15 The average of our four independent diene double bonds, 1.342 Å, is normal.

The difference in conformation of I and II, compared to V, is also reflected in the dihedral angles formed by the phenyl rings with the diene double bonds, as given in Table VII. As in V, all of the (13) G. A. Dooradian, H. H. Freedman, R. F. Bryan, and H. P. Weber,

J. Amer. Chem. Soc., 92, 399 (1970). (14) D. C. Hodgkin, B. M. Rimmer, J. D. Dunitz, and K. N. Trueblood,

J. Chem. Soc., 4945 (1963).
 (15) R. F. Bryan, private communication. Values refer, respectively,

 (15) K. F. Bryan, private communication. Values refer, respectively, to the *cis,trans*-dichloro- and the *trans,cis*-monochlorotetraphenylbutadienes, which have respective skew angles of 66 and 58°.
 (16) I. L. Karle and K. S. Dragonette, Acta Crystallogr., 19, 500 (1965).

Standard errors for C-C bonds are stated to be in the range 0.009-0.012 Å.

(17) K. Kuchitsu, T. Fukuyama, and Y. Morino, J. Mol. Struct., 1, 463 (1968).

phenyls are twisted well out of coplanarity, effectively precluding conjugation between the π systems. However, the mean dihedral angle of 52° in I and II is slightly less than the average angle of 58° in V.¹

The structures of these highly crowded dienes show some interesting features that may indicate the presence of strain in the ground state. The C(1)-Sn-C(5) angle is 116.5° in I and 117.1° in II, significantly larger than the tetrahedral angle of 109.5°. This angle may have opened to permit the vinyl halogen to pack between the C(1) and C(5) substituents on tin. We note that in V, the corresponding angle was opened to the very high value of 129.0° to allow the close Sn \cdots Br contact.

Significant (0.05-0.11 Å) distortions from planarity occur in the ethylenic moieties of I and II. These can be interpreted as twisting about the double bonds and are further evidence for strain. These effects occur in the same direction and are of approximately the same magnitude in the two independent structures, as seen in Table VII. For example, Sn and C(13) lie above and C(3) and C(7) fall below a least-squares plane (E) through the 1,2 double bond and its four substituent atoms. Similarly, the halogen atom and C(19) are above plane F (the 3,4 bond) while C(2) and C(25) lie below. Deviations from planarity in the five phenyl rings (A-D, G) are much smaller.

In general bond distances in this system are normal; the Sn-C(sp³) bonds average 2.17 Å¹⁸ and the Sn-C-(sp²) bonds 2.14 Å, while the C-X bonds are 1.728 Å (Cl) and 1.909 Å (Br). The eight C-C₆H₅ bond distances average 1.474 Å. Of the 60 independent determinations of C-C bond lengths in phenyl groups, only two appear to be anomalous (more than 3σ from the accepted value 1.396 Å), viz C(27)-C(28) and C(33)-C(34) of structure I.

(18) E. O. Schlemper and W. C. Hamilton, Inorg. Chem., 5, 995 (1966);
 N. W. Alcock and R. E. Timms, J. Chem. Soc. A, 1873, 1876 (1968).

						Observei	O AND	CA	LCULATE	ST ST	RUCTURE	FAC	TORS	IN]	ELECTRON	S FOR	х	-	Br					
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TABLE IIIB

TABLE IV

Root-Mean-Square Amplitudes of Thermal Motion with Direction $Cosines^{a,b}$

Atom			
Sn (X = C1)	0.1973 (13)	0.2125 (9)	0.2264(12)
	0.398 (51), 0.661 (26), 0.636 (17)	-0.914 (23), 0.339 (72), 0.220 (47)	-0.070 (66), -0.669 (21), 0.740 (14)
C1	0.1703 (38)	0.2302 (35)	0.2840 (32)
	0.783 (33), 0.396 (28), -0.479 (31)	-0.621 (35), 0.452 (40), -0.641 (36)	-0.037 (37), 0.799 (23), 0.600 (31)
Sn (X = Br)	0.2001 (17)	0.2135 (17)	0.2272 (21)
	0.335 (89), 0.787 (60), 0.518 (40)	-0.787(82), 0.536(103), -0.304(72)	-0.518(83), -0.306(72), 0.799(29)
Br	0.1831 (29)	0.2386(27)	0.2851 (20)
	0.740(25), 0.472(21), -0.479(21)	-0.670(23), 0.459(32), -0.583(30)	-0.055 (34), 0.753 (18), 0.656 (21)

^a Standard errors referred to the last significant digit are given in parentheses. ^b Direction cosines are referred to a, b, and c, respectively.

TABLE V

Bond Distances $(\text{\AA})^{a}$

Atoms	$\mathbf{X} = \mathbf{C}\mathbf{i}$	X = Br	Atoms	$\mathbf{X} = \mathbf{C}\mathbf{I}$	X = Br
$Sn \cdots X$	4.284(3)	4.346(2)	C(16) - C(17)	1.373(14)	1.373(20)
Sn-C(1)	2.148 (8)	2.156(12)	C(17)-C(18)	1.378(13)	1.400(18)
Sn-C(5)	2.180(11)	2.188(15)	C(18)-C(13)	1.411(12)	1.421(16)
Sn-C(6)	2.154(10)	2.165(13)	C(19)-C(20)	1.402(14)	1.432(18)
Sn-C(31)	2.116(9)	2.141(13)	C(20)-C(21)	1.396(12)	1.447(17)
C(4)-X	1.728(9)	1,909 (12)	C(21)-C(22)	1.384(17)	1.361(21)
C(1)-C(2)	1.328(11)	1.344(16)	C(22)-C(23)	1.402(15)	1,400(20)
C(2)-C(3)	1.498 (11)	1.505(16)	C(23)-C(24)	1.440(15)	1.458(20)
C(3) - C(4)	1.343(11)	1.353 (16)	C(24)-C(19)	1.352(14)	1.355(18)
C(1)-C(7)	1.466(11)	1.460(16)	C(25)-C(26)	1.434(13)	1.428(17)
C(2)-C(13)	1.492(12)	1.473(17)	C(26)-C(27)	1,407(12)	1.408(17)
C(3)-C(19)	1.487(11)	1.472(15)	C(27)-C(28)	1.327(13)	1.369 (18)
C(4)-C(25)	1.470(12)	1.468(17)	C(28)C(29)	1.409 (15)	1.379(19)
C(7)-C(8)	1.380(12)	1,393 (16)	C(29)-C(30)	1.415(14)	1.409(18)
C(8) - C(9)	1.409(14)	1.414 (19)	C(30)-C(25)	1.424(12)	1.407(17)
C(9)-C(10)	1.362(14)	1.385(18)	C(31)-C(32)	1.395(12)	1.385(16)
C(10)-C(11)	1.357(14)	1.374 (18)	C(32)-C(33)	1.415(14)	1.399 (18)
C(11)-C(12)	1.395(14)	1.425(18)	C(33)-C(34)	1,324(15)	1,359(20)
C(12)-C(7)	1.396 (13)	1.400(17)	C(34)-C(35)	1.375(16)	1.402(22)
C(13)-C(14)	1.395(12)	1.394(17)	C(35)-C(36)	1.405(16)	1.385(21)
C(14)-C(15)	1.421(14)	1.414 (19)	C(36)-C(31)	1.383(12)	1,396 (18)
C(15)-C(16)	1.362(14)	1.358(19)			

^a Standard errors referred to the last significant digit are given in parentheses.

TABLE VI

BOND ANGLES (DEG)^a

Atoms	X = Ci	X = Br	Atoms	X = Cl	X = Br
		Angles	at Tin		
C(1)-Sn-C(5)	116.5(4)	117.1(5)	C(6)-Sn-C(31)	104.9(4)	105.8(5)
C(1)-Sn-C(6)	109.5(4)	109.4(5)	$X \cdots Sn-C(1)$	56.0(2)	55.2(3)
C(1)-Sn- $C(31)$	109.3 (3)	108.4(5)	$X \cdots Sn-C(5)$	62.0(3)	63.8(4)
C(5)-Sn-C(6)	105.5(4)	104.5(6)	$X \cdots Sn-C(6)$	112.7(3)	110.5(4)
C(5)-Sn-C(31)	110.5(4)	110.9(5)	$X \cdots Sn-C(31)$	142.3 (2)	143.4 (3)
		Angles at Cl	nain Carbons		
Sn-C(1)-C(2)	124.8(6)	124.6(9)	C(2)-C(3)-C(4)	122.2(8)	121.2(11)
Sn-C(1)-C(7)	113.0(6)	112.5(8)	C(2)-C(3)-C(19)	116.5(7)	117.4 (10)
C(2)-C(1)-C(7)	122.1(8)	123.0(11)	C(4)-C(3)-C(19)	121.2(8)	121.3 (11)
C(1)-C(2)-C(3)	122.1(8)	122.1(11)	Br-C(4)-C(3)	119.8(7)	118.5(9)
C(1)-C(2)-C(13)	123.7(8)	122.3(11)	Br-C(4)-C(23)	112.6(6)	114.4 (9)
C(3)-C(2)-C(13)	114.1(7)	115.4(11)	C(3)-C(4)-C(25)	127.5(8)	126.7(11)
		Angles at R	ing Carbons		
C(1)-C(7)-C(8)	121.3 (8)	120.5(12)	C(20)-C(21)-C(26)	119.6(12)	120.8(15)
C(1)-C(7)-C(12)	119.8(8)	119.9(12)	C(21)-C(22)-C(27)	121.4(11)	121.5(15)
C(8)-C(7)-C(12)	118.8 (8)	119.5(12)	C(22)-C(23)-C(28)	117.5(10)	118.2(14)
C(7)-C(8)-C(9)	119.4 (9)	120.7(13)	C(23)-C(24)-C(19)	120.8(9)	121.0 (13)
C(8)-C(9)-C(10)	120.7(10)	119,1(14)	C(4)-C(25)-C(26)	121.9 (8)	120.9 (12)
C(9)-C(10)-C(11)	120.5(11)	120.8(15)	C(4)-C(25)-C(30)	117.7(8)	119.0(12)
C(10)-C(11)-C(12)	119.9(11)	120.4(15)	C(26)-C(25)-C(30)	120.4(9)	120.2(12)
C(11)-C(12)-C((7))	120.5(9)	119.0 (14)	C(25)-C(26)-C(27)	119.3 (9)	118.8(12)
C(2)-C(13)-C(14)	121.5(8)	122.9(12)	C(26)-C(27)-C(28)	119.8(9)	119.4 (13)
C(2)-C(13)-C(18)	121.3 (8)	120.1(12)	C(27)-C(28)-C(29)	123.3(10)	123.0(14)
C(14)-C(13)-C(18)	117.1 (8)	117.0(13)	C(28)-C(29)-C(30)	119.8(10)	119.2(14)
C(13)-C(14)-C(15)	120.3 (9)	120.8(13)	C(29)-C(30)-C(25)	117.3(9)	119.3 (13)
C(14)-C(15)-C(16)	120.4(10)	120.6(15)	Sn-C(31)-C(32)	118.2(6)	117.5(9)
C(15)-C(16)-C(17)	119.8(10)	120.6(15)	Sn-C(31)-C(36)	121.9(7)	122.2(10)
C(16)-C(17)-C(18)	120.8(10)	119.8(14)	C(32)-C(31)-C(36)	119.9(9)	120.3(13)
C(17)-C(18)-C(13)	121.4 (9)	121.1 (13)	C(31)-C(32)-C(33)	118.9(9)	120.6 (13)
C(3)-C(19)-C(20)	119.3 (8)	118.4(12)	C(32)-C(33)-C(34)	121.8(11)	119.4(15)
C(3)-C(19)-C(24)	120.0(8)	121.1(12)	C(33)-C(34)-C(35)	119.1 (12)	120.3 (16)
C(20)-C(19)-C(24)	120.7 (8)	120.5(11)	C(34)-C(35)-C(36)	122.3 (11)	121.1(16)
C(19)-C(20)-C(25)	120.0(11)	118.0(13)	C(35)-C(36)-C(31)	118.0 (10)	118.3(15)

^e Central atom is vertex. Standard errors in 0.1° units are in parentheses.

				<i>P</i>	L. Least Squar	es-Planes"			
Atom		A		в	с	———— Plane —— D	E	F	G
1		C(1)		$\mathbf{C}(2)$	C(3)	C(4)	Sn	х	Sn
2		$\tilde{C}(7)$		C(13)	C(19)	C(25)	$\mathbf{C}(1)$	$\mathbf{C}(2)$	C(31)
3		C(8)		C(14)	$\mathbf{C}(20)$	C(26)	$\mathbf{C}(2)$	$\mathbf{C}(3)$	C(32)
4		$\mathbf{C}(9)$		C(15)	$\mathbf{C}(21)$	C(27)	C(3)	C(4)	C(33)
5		$\mathbf{C}(10)$		C(16)	C(22)	C(28)	C(7)	C(19)	C(34)
ß		$\mathbf{C}(11)$		C(17)	C(23)	C(29)	C(13)	C(25)	C(35)
9 7		C(12)		C(18)	C(24)	$\mathbf{C}(30)$	0(10)	0(20)	C(36)
					$\mathbf{X} = \mathbf{C}$	21			
m_1		-8.690		15.467	-7.340	6.554	9.410	-3.718	9.215
mo		5.198		1.458	10.282	10.959	7.050	9.394	-1.379
ma		11.045		-1.370	-3.622	0.339	-8.464	9.029	12.420
d		3.509		6.620	-1.817	6.301	3.249	5.448	8.921
$\Delta d(\text{atom } 1)$		-0.027		-0.009	-0.007	0.020	0.053	0.082	-0.006
$\Delta d(\text{atom } 2)$		0.019		-0.009	-0.003	-0.013	0.006	-0.110	0.011
$\Delta d(\text{atom } 3)$		0.014		0.036	-0.001	-0.009	-0.009	0.025	-0.011
$\Delta d(\text{atom } 4)$		-0.007		-0.020	0.006	0.002	-0.062	0.025	0.010
$\Delta d(\text{atom } 5)$		-0.006		-0.016	0.001	0.006	-0.063	0.084	-0.003
$\Delta d(\text{atom } 6)$		-0.017		0.025	-0.019	0.014	0.075	-0.106	-0.013
$\Delta d(\text{atom 7})$		0.025		-0.008	0.025	-0.020			0.011
					X = B	Br			
m_1		-8.659		15.630	-7.435	6.885	9.464	-3.941	9.260
m_2		5.106		1.705	10.287	10.856	7.112	9.398	-1.408
ma		11.258		-1.729	-3.544	0.136	-8.477	8.938	12.515
d		3.527		6.688	-1.866	6.343	3.310	5.268	8.977
$\Delta d(\text{atom } 1)$		-0.027		-0.013	-0.004	0.015	0.059	0.062	0.007
$\Delta d(\text{atom } 2)$		0.001		-0.006	-0.004	0.001	-0.004	-0.101	-0.007
$\Delta d(\text{atom } 3)$		0.034		0.014	-0.002	-0.010	-0.018	0.026	-0.017
$\Delta d(\text{atom } 4)$		-0.024		0.009	0.008	-0.005	-0.059	0.042	0.017
$\Delta d(\text{atom } 5)$		0.006		-0.026	-0.004	0.015	-0.059	0.071	-0.000
$\Delta d(atom 6)$		-0.026		0.006	-0.009	0.006	0.082	-0.099	-0.008
$\Delta d (\text{atom } 7)$		0.035		0.017	0.016	-0.021			0.008
			в.	Dihedral	Angles between	n Least-Squares	s Planes		
	Plane 1			Plane 2		Angle $(X = Cl)$		Angle (X = Br)	
	Α			E		61° 56′		62°4′	
	в			\mathbf{E}		44° 31′		43° 7'	
	С			F		50° 17′		49° 21′	
	D			F		51° 44′		53°5'	
	E			\mathbf{F}		89° 41′		90° 0'	

TABLE VII

^a These planes are defined by the equation $m_1x + m_2y + m_3z = c$. The distances Δd of the atoms from this plane are in ångströms.



Figure 2.—Molecular packing in a unit cell of (4-chloro-1,2,3,4-tetraphenylbutadienyl)dimethylphenyltin. The view is down the y axis with x horizontal and z vertical.

Figure 2 shows¹¹ the molecular packing and a unit cell outline for I. We are viewing down y, with x horizontal and z vertical. There are a total of 11 intermolecular C···C contacts and one C···Cl contact less than 3.7 Å; none of these is unusually short.

Most of these shorter contacts (Å) arise via the screw diad: C(27)-C(17), 3.560; C(27)-C(12), 3.575; C-(26)-C(35), 3.645; C(28)-C(16), 3.668; C(5)-C(14), 3.670; C(27)-C(35), 3.675; C(33)-C(16), 3.675; C-(32)-C(15), 3.676. The remaining close contacts (Å)

originate through the *a* glide: C(29)-Cl, 3.579; C-(34)-C(6), 3.608; C(17)-C(9), 3.618; C(35)-C(6), 3.691.

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The Crystal Structure of Tris(2-aminoethyl)aminochlorozinc(II) Tetraphenylborate¹

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The crystal structure of tris(2-aminoethyl)aminochlorozinc(II) tetraphenylborate has been determined from an X-ray study of a single-crystal specimen. The monoclinic cell, space group $P2_1/c$, with $a = 13.76 \pm 0.04$ Å, $b = 10.33 \pm 0.03$ Å, $c = 20.35 \pm 0.06$ Å, and $\beta = 95.0 \pm 0.2^{\circ}$, contains four formula units; the calculated X-ray density is 1.30 g/cm^3 . The structure was refined to a conventional R factor of 0.041 for 2193 structure factors. The structure consists of a $Zn(C_2H_4NH_2)_3NCl$ cation and a $(C_6H_5)_4B$ anion. The cation has approximate C_8 symmetry. Within the cation the Zn atom is pentacoordinated to one chlorine and four nitrogen atoms in a trigonal-bipyramidal configuration.

Introduction

Although the coordination number 5 is generally regarded as an unusual one for first-row transition metals, a steadily increasing number of five-coordinated complexes are being described in the literature. In particular, the quadridentate ligands tris(2-dimethylaminoethyl)amine and tris(2-aminoethyl)amine appear to form a variety of five-coordinated complexes with the first-row transition metal ions from manganese(II) to zinc(II). These ligands are more conveniently designated Mestren and tren, respectively. In general, these may be formulated as [M^{II}Me₆trenX]Y or [M^{II}trenX]Y. The relative stability of five-coordination among these metals is favored in the order (Co, Cu, Zn) > (Fe, Ni) > Mn.² Because of the increased bulkiness of Mestren, it forms more stable five-coordinated complexes than tren. Mestren complexes have been described, for which M = Mn, Fe, Co, Ni, Cu, or Zn, and for which X = Y = Cl, Br, I, NO₃, or ClO₄.^{3,4} Much physical evidence, including conductivity, spectral, and magnetic measurements, indicated that these complexes are five-coordinated. In addition, crystal structure determinations of [Cu(tren)(NCS)]SCN,5 [Co(Mestren)Br]Br, and [Cu(Mestren)Br]Br⁶ reveal that the metal atoms are indeed five-coordinated and situated nearly at centers of slightly distorted trigonal bipyramids. A recent report⁷ on the structure of Zn(tren)(NCS)(SCN) also shows trigonal-bipyramidal symmetry.

More recently, a series of complexes has been pre-

and P. L. Orioli, Acta Crystallogr., Sect. B, 24, 595 (1968). (7) G. D. Andreetti, P. C. Jain, and E. C. Lingafelter, J. Amer. Chem. Soc.,

91, 4112 (1969).

pared, [Zn(tren)X]Y, for which X = Cl, Br, or I and Y = X, ZnX_3 , or $B(C_6H_5)_{4.8}$ We report here the crystal structure of the five-coordinated complex $[Zn(C_2-H_4NH_2)_3NCl]B(C_6H_5)_4$.

Experimental Section

Dr. L. V. Interrante kindly supplied us with some wellformed, colorless prisms of $[Zn(tren)Cl]B(C_6H_6)_4$, which were suitable for the structural analysis. The determination of the space group and cell dimensions was made using the precession technique and molybdenum radiation (Mo K α_1 , $\lambda 0.70926$ Å). A General Electric XRD-5 X-ray diffraction apparatus equipped with a molybdenum X-ray tube, a scintillation counter, a pulse height discriminator, and a quarter-circle Eulerian-cradle type of goniostat was used to collect the intensity data. The Xray tube was operated at 45 kV and 20 mA; a 0.003-in. thick Zr filter was used on the receiving slit. The crystal was oriented such that the c axis was parallel to the ϕ axis of the instrument.

A total of 2692 independent intensities were measured, of which 233 were recorded as having zero intensity. A stationary-crystal, stationary-counter technique with a 10-sec count for every reflection was used. The diffractometer was set at a 4° takeoff angle to the tube. The maximum 2 θ angle was 40° [$(\sin \theta)/\lambda =$ 0.596]. Background was plotted as a function of 2 θ and these values were used for most of the intensities; in the cases where background was seriously affected by streaking, individual backgrounds were measured. The absorption parameter is 9.9 cm⁻¹. No absorption correction could be made because the crystal was lost and its dimensions are unknown. The Lorentz and polarization corrections were applied to the data. No extinction correction was found necessary.

Fourier, least-squares, and distance calculations were performed using our own unpublished programs. The full-matrix least-squares program, which is a modification of an early unpublished version of one given us by P. Gantzel, R. Sparks, and K. Trueblood, minimizes the function $\Sigma w(|F_o| - |F_o|)^2 / \Sigma w F_o^2$; F_o and F_o are the observed and calculated structure factors, respectively, and w is the weighting factor. Atomic scattering factors^{9,10} for neutral zinc, chlorine, boron, carbon, nitrogen, oxygen, and hydrogen were used. Both the real and imaginary

⁽¹⁾ Work done under the auspices of the U. S. Atomic Energy Commission.

⁽²⁾ M. Ciampolini and P. Paoletti, Inorg. Chem., 6, 1261 (1967).

⁽³⁾ M. Ciampolini and N. Nardi, *ibid.*, 5, 41 (1966).
(4) M. Ciampolini and N. Nardi, *ibid.*, 5, 1150 (1966).

 ⁽⁴⁾ M. Clampolini and N. Nardi, 50^a., 9, 1100 (1966).
 (5) P. C. Jain and E. C. Lingafelter, J. Amer. Chem. Soc., 89, 724 (1967).

⁽⁶⁾ M. DiVaira and P. L. Orioli, Inorg. Chem., 6, 955 (1967); M. DiVaira

⁽⁸⁾ L. V. Interrante, Inorg. Chem., 7, 943 (1968).

⁽⁹⁾ D. T. Cromer and J. T. Waber, Acta Crystallogr., 18, 104 (1965).

⁽¹⁰⁾ R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., 42, 3175 (1965).