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### Application of a Stereochemical Model to the Mononuclear Complexes of Tin<sup>1</sup>

Robert F. Zahrobsky

Contribution from the Department of Chemistry,  
University of Illinois at Chicago Circle, Chicago, Illinois 60680.  
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**Abstract:** A stereochemical model based on nonbonded intramolecular van der Waals interactions is presented and is shown to account for the observed bond angles and bond lengths in monodentate complexes which have tin as a central atom. The model is applied to several mononuclear complexes of tin that have been studied by X-ray diffraction:  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ ,  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ ,  $\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{SO}$ ,  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$ ,  $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ ,  $(\text{CH}_3)_2\text{SnCl}_3^-$ ,  $(\text{CH}_3)_2\text{SnCl}_2$ , and  $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ . The bond angles calculated from the model for the octahedral complexes generally agree with observed bond angles within the limits of experimental error, while the bond angles calculated for the five- and four-coordinate species provide a semiquantitative approximation of the molecular geometry. The generality of the approach indicates that the method may be valid for estimating molecular geometry around central atoms other than tin, in cases where appreciable intramolecular nonbonded interactions exist. In terms of the model, a means of predicting the isomer of a complex which is most likely to exist is also discussed.

Methods of calculating and constructing models of molecular geometry to predict the arrangement of atoms around a central atom differ considerably in their approach and level of sophistication. The models vary from highly mathematical quantum mechanical or "molecular mechanics" approaches<sup>2</sup> to simple geometric methods<sup>3</sup> which require little or no calculation. It has been pointed out<sup>4</sup> that the simpler models which have met with success in predicting the shapes of molecules have been approached from one of two points of view; namely, the bond angles and bond lengths around a central atom are governed either by nonbonded atom-atom interactions or by the distribution and interaction of electron pairs in the valence shell of the central atom. Presented here is a stereo-

chemical model which is essentially based on intramolecular nonbonded interactions of atoms bonded to a central atom.

The molecular complexes of tin are known to exist in a wide variety of highly distorted tetrahedral, trigonal-bipyramidal, and octahedral geometries.<sup>5</sup> Hence, these molecules provide an ideal system for testing a molecular model which attempts to semiquantitatively predict the shapes of molecules. The major emphasis in explaining the shapes of these molecules has generally been placed on the electronic properties of the central atom. However, it will be shown that if it is assumed that the complexes of tin are stereochemically nonrigid, the shapes of these molecules are quantitatively and qualitatively consistent with a simple nonbonded interaction model.

#### Discussion

**The Model.** It is assumed that the strongest nonbonded interactions occur in a region around a central atom that may be represented by a sphere which has a

(1) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 16, 1970.

(2) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); (b) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *ibid.*, **47**, 3736 (1967); (c) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970).

(3) (a) R. J. Gillespie, *Can. J. Chem.*, **39**, 318 (1961); (b) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(4) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(5) R. S. Tobias, *Trans. N. Y. Acad. Sci., Ser. II*, **31**, 913 (1969).

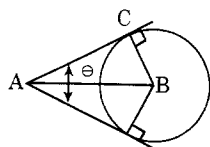


Figure 1. Construction of a steric angle,  $\theta$ , from covalent bond length and van der Waals radius.

radius approximately equal to the average donor atom central atom bond length and a center that is coincident with the central atom. It is also assumed that the geometry of a molecule may be determined by balancing the forces acting about this sphere, and that the van der Waals surfaces of the ligand atoms represent equipotential surfaces. Further, it is assumed that the nonbonded interactions may be minimized by arranging the donor atoms around the central atom such that the distances (or overlap) between the van der Waals surfaces of adjacent donor atoms are equalized. The model approximates this condition by assigning to each donor atom a solid angle, the size of which is a function of the donor atom–central atom bond distance and the van der Waals radius of the donor atom. These solid angles are then distributed around the central atom so that the distances (or overlap) between adjacent conic surfaces are equal. The solid angle representing a donor atom may be generated by considering the set of lines from a central atom, A, that are tangent to the van der Waals surface of a bonded ligand atom, B, as shown in Figure 1, where AB is the sum of the covalent radii and BC is the van der Waals radius of the donor atom. Then, the principal region of steric influence of a bonded ligand atom may be considered to lie within a “steric angle,”  $\theta$ , defined by  $\theta = 2 \arcsin(BC/AB)$ . Thus, this construction results in an invariant representation of donor atoms bonded to a particular central atom. By using the van der Waals radii<sup>6</sup> and covalent radii<sup>7</sup> found in the literature, the model may be applied to molecules of unknown structure.

The choice of a solid angle to represent bonded donor atoms is a matter of analytical convenience, and the approximation therein is consistent with the simplicity and semiquantitative nature of the method. An advantage of an angular representation is that the three-dimensional distribution of cones around a central point, or the distribution of angles in a cross-sectional plane of a molecule, is generally trivial and leads to a direct estimate of the bond angles in a molecule. Furthermore, a conic representation is convenient for expressing the change in the steric requirements of a donor atom as the donor atom–central atom bond length changes. Thus, the model may be readily adapted to molecules of known structure by substituting experimental bond lengths for the bond lengths derived from covalent radii while still preserving the essential parameter of the nonbonded interactions, the van der Waals radius of the donor atom. Finally, it may be noted that the representation of a donor atom by a solid angle is useful in predicting the steric effects of ligand atoms other than the donor.

(6) L. Pauling, “The Nature of the Chemical Bond,” 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(7) R. T. Sanderson, “Inorganic Chemistry,” Reinhold, New York, N. Y., 1967, p 74.

Table I. Covalent Radii and van der Waals Radii Used in This Work

| Element | Covalent radius, Å <sup>a</sup> | van der Waals radius, Å <sup>b</sup> |
|---------|---------------------------------|--------------------------------------|
| C       | 0.77                            | 2.0 (methyl group)                   |
| N       | 0.75                            | 1.5                                  |
| O       | 0.73                            | 1.4                                  |
| Cl      | 0.99                            | 1.8                                  |
| Sn      | 1.41                            |                                      |

<sup>a</sup> Reference 7. <sup>b</sup> Reference 6.

The values of the covalent<sup>7</sup> and van der Waals<sup>6</sup> radii used in this work are listed in Table I. Steric angles calculated from the data in Table I are listed in Table II.

Table II. Steric Angles of Ligand Atoms Computed from van der Waals Radii and Covalent Bond Lengths

| Central atom–donor atom | Steric angle, deg <sup>a</sup> |
|-------------------------|--------------------------------|
| Sn–C                    | 133 (methyl group)             |
| Sn–N                    | 88.0                           |
| Sn–O                    | 81.7                           |
| Sn–Cl                   | 97.3                           |

<sup>a</sup> There is no difference between the magnitudes of the solid steric angles used in three-dimensional representations and steric angles used in planar representations.

Ligand atoms other than the donor atom may exert a strong influence on molecular geometry and their effect may be assessed qualitatively and, in some cases, quantitatively by the present model. A ligand which contains more than one atom may be inspected in plausible orientations with respect to the donor atom–central atom bond, and the general criterion for estimating whether its nondonor atoms may potentially or actually affect molecular geometry, then, is that the van der Waals surfaces of the ligand atoms lie outside the steric angle. Ligands for which this condition exists may be divided into two categories—those in which the ligand atoms outside the steric angle lie on or very near the nonbonded interaction sphere of the donor atoms, and those in which the ligand atoms are considerably removed from the region of the donor atoms. If ligand atoms other than the donor lie in or near the nonbonded interaction sphere of the donor atoms, they affect the bond angles and bond lengths of donors around the central atom. Their effect may be taken into account with this stereochemical model by adjusting the size of the steric angle to include the van der Waals surfaces of the ligand atoms at the coordination sphere. In this present study, the hydrogen atoms of the methyl groups directly bonded to tin lie in this region and the steric angle has been increased to include their interaction. This was accomplished by assigning a symmetrical van der Waals radius of 2.0 Å to the methyl group and computing a steric angle based on this value. Ligands which produce the other category of steric effect might be typified by a bulky ligand, such as trimethylamine. The large methyl groups of this ligand are located beyond the coordination sphere of the donor atoms and will not affect the geometry of the central atom, unless a second bulky ligand is bonded to the central atom. When such is the case, it is found that the steric requirements of these ligands are usually so great that the bond angles around the central atom

Table III. Comparison of Calculated Bond Angles with Experimentally Determined Bond Angles in Octahedral Tin Complexes

| Compound   | Determination method      | Bond angles, deg |               |                   |                   |                   |               | Av exptl bond lengths, Å |      | Ref      |
|--|---------------------------|------------------|---------------|-------------------|-------------------|-------------------|---------------|--------------------------|------|----------|
|  |                           | O(1)Sn-O(2)      | Cl(1)Sn-Cl(2) | O(1)Sn-Cl(2)      | O(1)Sn-Cl(2)      | Cl(1)Sn-Cl(3)     | Cl(3)Sn-Cl(4) | Sn-Cl                    | Sn-O |          |
| SnCl <sub>4</sub> ·2(O donors) <sup>a</sup>  | Calcd from covalent radii | 82.2             | 97.8          | 90.0 <sup>e</sup> | 86.1              | 93.9              | 172.2         |                          |      |          |
|  | Exptl                     | 84.0             | 97.6          | 89.3 <sup>f</sup> | 87.8 <sup>f</sup> | 92.4 <sup>f</sup> | 172.7         | 2.38                     | 2.12 | <i>g</i> |
| SnCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> SO                                 | Calcd <sup>d</sup>        | 82.2             | 97.8          | 90.0 <sup>e</sup> | 86.2              | 93.8              | 172.4         |                          |      |          |
|  | Exptl                     | 81.9             | 100.1         | 89.1              | 84.1              | 95.1              |               | 2.39                     | 2.12 | <i>h</i> |
| SnCl <sub>4</sub> ·2Cl <sub>2</sub> SeO  | Calcd <sup>d</sup>        | 82.5             | 97.5          | 90.0 <sup>e</sup> | 86.2              | 93.8              |               |                          |      |          |
|  | Exptl                     | 78.3             | 103.0         | 89.4              | 83.0              | 95.6              |               | 2.33                     | 2.28 | <i>i</i> |
| SnCl <sub>4</sub> ·2Cl <sub>2</sub> PO   | Calcd <sup>d</sup>        | 77.3             | 102.7         | 90.0 <sup>e</sup> | 83.6              | 96.4              |               |                          |      |          |
|  | Exptl                     |                  |               |                   |                   |                   |               |                          |      |          |
| (CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·2(O donors) <sup>b</sup>            | Calcd from covalent radii | O(1)Sn-O(2)      | Cl(1)Sn-Cl(2) | O(1)Sn-Cl(2)      | O(1)Sn-C(1)       | Cl(1)Sn-C(1)      | C(1)Sn-C(2)   | Sn-Cl                    | Sn-O | Sn-C     |
|  | Exptl                     | 82.2             | 97.8          | 90.0 <sup>e</sup> | 86.1              | 93.9              | 172.2         |                          |      |          |
| (CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> SO | Calcd <sup>d</sup>        | 84.0             | 96.0          | 90.0              | 86.0              | 93.0              | 170.0         | 2.51                     | 2.35 | 2.08     |
|  | Exptl                     | 81.0             | 99.0          | 90.0 <sup>e</sup> | 85.0              | 95.0              | 171.0         |                          |      |          |
| SnCl <sub>4</sub> ·2(N donors) <sup>c</sup>  | Calcd from covalent radii | N(1)Sn-N(2)      | Cl(1)Sn-Cl(2) | N(1)Sn-Cl(2)      | N(1)Sn-Cl(3)      | Cl(1)Sn-Cl(3)     | Cl(3)Sn-Cl(4) | Sn-Cl                    | Sn-N |          |
|  | Exptl                     | 85.3             | 94.7          | 90.0 <sup>e</sup> | 87.7              | 92.3              | 175.4         |                          |      |          |
| SnCl <sub>4</sub> ·2CH <sub>3</sub> CN   | Calcd <sup>d</sup>        | 76.7             | 102.6         | 90.4              | 84.6              | 94.4              | 166.1         | 2.35                     | 2.33 | <i>k</i> |
|  | Exptl                     | 79.9             | 100.1         | 90.0 <sup>e</sup> | 84.9              | 95.1              | 169.8         |                          |      |          |

<sup>a</sup> Labels are consistent with **1**. <sup>b</sup> Labeled as **1**, except that C(1) and C(2) replace Cl(3) and Cl(4), respectively. <sup>c</sup> Labeled as **1**, except that N(1) and N(2) replace O(1) and O(2), respectively. <sup>d</sup> Calculated with steric angles obtained from averaged experimental bond lengths. <sup>e</sup> Necessarily 90° by the method of construction. <sup>f</sup> Experimental bond angles which are equivalent by C<sub>2v</sub> symmetry have been averaged. <sup>g</sup> Unpublished work of author. <sup>h</sup> Y. Hermodsson, *Acta Crystallogr.*, **13**, 656 (1960). <sup>i</sup> C.-I. Brändén, *Acta Chem. Scand.*, **17**, 759 (1963). <sup>j</sup> N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1257 (1970). <sup>k</sup> M. Webster and H. E. Blayden, *ibid.*, **A**, 2443 (1969).

cannot be widened sufficiently to permit the bulky ligands to assume an unhindered cis relationship without causing serious overlap between van der Waals surfaces of the donor atoms of the other ligands. Thus, the repulsive interactions are best minimized by the two bulky ligands assuming a trans relationship. Although the model calculation could be carried out for an assumed cis configuration, the predicted angles would certainly not be valid. Therefore, in application of the model to molecules with bulky ligands, some caution is advised. Further reference to both types of ligands is given in the text.

The stereochemical model may be constructed by the following procedure. (1) Select a particular geometric isomer of a molecule and, as an initial approximation, consider the donor atoms around the central atom as occupying regular polyhedral sites. (The subsequent steps may be applied to each of the recognizable isomeric configurations of a molecule.) (2) Assign each ligand atom a size in accord with its van der Waals radius. (3) Consider the donor atom of each ligand to be at a distance from the central atom given by the sum of donor atom and central atom covalent radii. (Experimental bond lengths may be substituted here for the analysis of molecules of known structure.) (4) Construct a steric angle for each donor atom based upon the donor atom–central atom bond distance and the van der Waals radius of the donor atom. (5) Consider the region with the strongest nonbonded interactions as a sphere with a radius equal to the average donor atom–central atom bond length. Examine the plausible orientations of the individual ligands to determine whether the van der Waals surfaces of any non-donor ligands lie on or in this sphere. (6) Estimate an increased size for the steric angles of ligands which have stereochemically active nondonor atoms, so that the

steric angle encompasses the van der Waals surfaces of any nondonor ligand atoms which lie in the sphere of strongest nonbonded interactions. (7) Distribute the steric angles around the central atom such that the distances (or overlap) between adjacent conic surfaces are equalized. This may be facilitated by seeking a solution which preserves any apparent molecular symmetry. (This three-dimensional distribution of different-sized cones with apices at a common point usually does not have an exact mathematical solution. Approximate solutions for the octahedral complexes were readily obtained by separating the three-dimensional problem into three two-dimensional analyses. Solutions for the four-coordinate molecules were obtained from a mechanical model consisting of a sphere upon which were distributed four circles. The circumferences of these circles correspond to the locus of points produced on the sphere surface by the intersection of the four solid steric angles which radiate from the center of the sphere.)

In the following three sections of the Discussion, the above model will be used to (1) calculate the bond angles around the central tin atom in several mononuclear monodentate complexes, (2) qualitatively predict variations in the central atom–donor atom bond lengths in tin complexes, and (3) provide a method or rationale for explaining the existence of only certain isomers in terms of the steric effects around a central tin atom.

**Bond Angles in Mononuclear Tin Complexes.** A simple determination of the distorted octahedral arrangement of donor atoms around a central atom may be accomplished by considering three mutually perpendicular planes, each of which cuts through the central atom and four donor atoms. The distribution of four steric angles may be analyzed separately in the three planes and then combined to form a three-di-

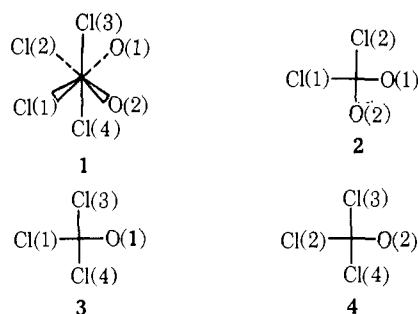


Figure 2. The octahedral geometry and its representation by three planes through the central atom.

mensional composite which gives an adequate representation of the molecule. This technique is applied to six-coordinate complexes which, for the purposes of this paper, will be referred to as octahedral.

Table III shows the results of the model calculation on the monodentate six-coordinate complexes of tin for which experimental bond angles have been determined.<sup>8</sup> For each of these molecules, bond angles have been calculated from steric angles derived both from experimental bond lengths and bond lengths equal to the sum of the covalent radii of the donor atom and central atom.

For illustrative purposes, the details of the calculation (using the sum of covalent radii for bond lengths) for the cis-octahedral  $\text{SnCl}_4 \cdot 2(\text{O donors})$  complexes listed in Table III will be described. In terms of the present model, these complexes are sterically equivalent, since they all involve the placement of four chlorine atoms and two cis oxygen atoms around a central tin atom. Figure 2 illustrates the cis-octahedral geometry 1, which is represented by the planar cross sections 2, 3, and 4, each of which contains the central tin atom and four donor atoms.

The evenly spaced planar distribution of two tin-chlorine and two tin-oxygen steric angles in a cis configuration as shown in 2 results in an  $\text{O}(1)\text{-Sn-O}(2)$  bond angle of  $82.2^\circ$  and a  $\text{Cl}(1)\text{-Sn-Cl}(2)$  bond angle of  $97.8^\circ$ . The distribution of three tin-chlorine and one tin-oxygen steric angle in plane 3 results in  $\text{Cl}(3)\text{-Sn-O}(1)$  and  $\text{Cl}(4)\text{-Sn-O}(1)$  bond angles of  $86.1^\circ$  and  $\text{Cl}(1)\text{-Sn-Cl}(3)$  and  $\text{Cl}(1)\text{-Sn-Cl}(4)$  bond angles of  $93.9^\circ$ . The results from plane 4 are identical with those obtained for plane 3. The  $\text{Cl}(3)\text{-Sn-Cl}(4)$  bond angle calculated from either plane 3 or 4 is  $173.3^\circ$ ; however, in constructing a three-dimensional composite, the  $\text{Cl}(3)$  and  $\text{Cl}(4)$  atoms should be construed as lying neither in plane 3 nor plane 4. By a symmetrical construction, the  $\text{Cl}(3)$  and  $\text{Cl}(4)$  atoms lie in a plane which bisects the  $\text{O}(1)\text{-Sn-O}(2)$  bond angle and is perpendicular to plane 2. It will be noted that the bond angles calculated for  $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$  are identical with the bond angles calculated from covalent bond lengths for the tin(IV)-chloride complexes with oxygen donors. This occurs because both species have the same molecular symmetry and an identical distribution of atoms in plane 2, conditions which are sufficient to make the bond angles identical by the method of calculation.

(8) The *trans,trans,trans*- $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2(\text{pyridine } N\text{-oxide})$  complex represents a trivial case, since the bond angles are determined by the symmetrical arrangement of the ligands.

An examination of Table III reveals that the present nonbonded interaction model predicts bond angles which are in good agreement with experiment. Moreover, it will be noted that when experimental bond lengths are employed to calculate steric angles, the agreement is generally within experimental error, which in these cases corresponds to a standard deviation of about  $1^\circ$ . The generalization that the octahedral bond angles around a central atom are related qualitatively to the van der Waals radii of the ligand atoms and the experimental bond lengths<sup>9</sup> is extended by the present model, which shows that a quantitative relationship also exists.

The rather large discrepancy between the observed bond angles and the bond angles calculated from steric angles based on covalent radii in  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$  may be attributable to the fact that the effective van der Waals radius of an atom depends upon the orientation of the contact relative to the covalent bond or bonds formed by that atom.<sup>6</sup> In particular, for the donor atoms under consideration, the van der Waals radius of a nitrile nitrogen atom may well exhibit the greatest amount of directional dependence, since a large amount of its electron density is involved in bonding. It should be possible to calculate an improved "intramolecular van der Waals distance" for a contact approximately perpendicular to the tin-nitrogen bond by examining the bond angles, bond lengths, and steric angles in an octahedral complex such as  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$ . Taking, as a reference, an intramolecular nonbonded radius of a chlorine atom as equal to the van der Waals radius of a chlorine atom, the analytical procedure may be altered so that an effective steric angle for the nitrogen donor atoms may be computed. Then, from the observed  $\text{Sn-N}$  bond length, an intramolecular nonbonded radius may be calculated for the contacts approximately perpendicular to the nitrogen bond axis. This calculation results in a nonbonded radius of  $1.40 \text{ \AA}$  for the bonded nitrile nitrogen atom. This value not only necessarily leads to a more acute  $\text{N-Sn-N}$  bond angle, but also produces a sum of steric angles for  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$  which is in better agreement with the observed  $\text{Sn-Cl}$  bond lengths (see Table V). The use of a nonbonded radius of  $1.40 \text{ \AA}$  for a nitrile nitrogen atom also improves the agreement with experiment for the observed bond angles in  $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$  (see Table IV). This procedure could conceivably produce a self-consistent set of radii which are more accurate than van der Waals radii in estimating the effects of nonbonded interactions on molecular geometry.

Bond angles in five- and four-coordinate species may also be estimated by the model. The  $(\text{CH}_3)_2\text{SnCl}_3^-$  anion<sup>10</sup> has two methyl groups and one chlorine atom in the equatorial plane with a  $\text{C-Sn-C}$  bond angle of  $140^\circ$  ( $\sigma = 2^\circ$ ). The arrangement of ligands in the equatorial plane based on the distribution of one tin-chlorine and two tin-methyl steric angles predicts a  $\text{C-Sn-C}$  bond angle of  $132^\circ$ , which is slightly outside the limits of experimental error. Two four-coordinate tin molecules,  $(\text{CH}_3)_2\text{SnCl}_2$  and  $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ , have donor atoms which form highly distorted tetrahedra around the central atom.<sup>11,12</sup> Using steric angles

(9) I. Lindqvist, "Inorganic Adduct Molecules of Oxo-compounds," Academic Press, New York, N. Y., 1963.

(10) F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968).

**Table IV.** Comparison of Estimated and Experimental Bond Angles in Four-Coordinate Tin Complexes

| Compound   | Determination method | Bond angles, deg        |                          |
|--|----------------------|-------------------------|--------------------------|
|  |                      | Cl-Sn-Cl                | C-Sn-C                   |
| (CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>    | Exptl                | 98.8 ( $\sigma = 1.8$ ) | 141.9 ( $\sigma = 4.2$ ) |
|  | Estd                 | 95 ( $\pm 3$ )          | 127 ( $\pm 3$ )          |
| (CH <sub>3</sub> ) <sub>2</sub> Sn(NCS) <sub>2</sub> |                      | N-Sn-N                  | C-Sn-C                   |
|  | Exptl                | 84.1 ( $\sigma = 1.6$ ) | 145.9 ( $\sigma = 1.4$ ) |
|  | Estd                 | 86 ( $\pm 3$ )          | 132 ( $\pm 3$ )          |
|  | Estd <sup>a</sup>    | 84 ( $\pm 3$ )          | 136 ( $\pm 3$ )          |

<sup>a</sup> Estimate made with a van der Waals radius for nitrogen of 1.40 Å.

based on covalent radii, bond angles estimated from the model are compared in Table IV with the experimentally determined values. The estimated values of the bond angles in these four-coordinate molecules show appreciable deviation from the experimental values; however, they do provide a semiquantitative approximation of the distortions that may be expected in these molecules. The fact that the predictive value of the model diminishes as the coordinate number decreases is consistent with the notion that nonbonded interactions become less important in the determination of molecular geometry as the nonbonded intramolecular distances increase.

**Bond Lengths in Tin Complexes.** Variations in bond lengths to the central atom, regardless of the electronic properties of the attached ligands, may be correlated with the magnitude of the nonbonded interactions in the donor-atom coordination sphere, as measured by the sum of steric angles based on covalent radii. This is demonstrated in Table V, wherein a comparison of

**Table V.** Comparison of Averaged Sn-Cl Bond Lengths with the Sum of the Steric Angles in Octahedral Tin Complexes

| Tin complex  | Av Sn-Cl bond length, Å | Sum of steric angles, deg | Ref      |
|--|-------------------------|---------------------------|----------|
| SnCl <sub>3</sub> ·2POCl <sub>3</sub>  | 2.33                    | 553                       | <i>d</i> |
| SnCl <sub>4</sub> ·2CH <sub>3</sub> CN   | 2.35                    | 565 <sup>b</sup>          | <i>e</i> |
| SnCl <sub>4</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> SO                                 | 2.38                    | 553                       | <i>f</i> |
| SnCl <sub>4</sub> ·2SeOCl <sub>2</sub>   | 2.39                    | 553                       | <i>g</i> |
| SnCl <sub>6</sub> <sup>2-</sup>  | 2.42                    | 584                       | <i>h</i> |
| (CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·2(CH <sub>3</sub> ) <sub>2</sub> SO | 2.51                    | 624 <sup>c</sup>          | <i>i</i> |
| (CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ·2pyr-NO <sup>a</sup>                | 2.58                    | 624 <sup>c</sup>          | <i>j</i> |

<sup>a</sup> pyr-NO = pyridine *N*-oxide. <sup>b</sup> A van der Waals radius for nitrogen of 1.4 Å, instead of 1.5 Å, reduces this value to 551°.

<sup>c</sup> The repulsive interactions exerted on the chlorine atoms in (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>·2pyr-NO are slightly greater than the interactions in (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>·2(CH<sub>3</sub>)<sub>2</sub>SO, owing to differences in isomeric configuration. <sup>d</sup> C.-I. Branden, *Acta Chem. Scand.*, **17**, 759 (1963). <sup>e</sup> M. Webster and H. E. Blayden, *J. Chem. Soc. A*, 2443 (1969). <sup>f</sup> A. Hansson and O. Brunge, private communication quoted by I. Lindqvist, "Inorganic Adduct Molecules of Oxo-compounds," Academic Press, New York, N. Y., 1963, and unpublished work of the author. <sup>g</sup> Y. Hermodsson, *Acta Crystallogr.*, **13**, 656 (1960). <sup>h</sup> G. Engel, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **90**, 341 (1935). <sup>i</sup> N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 2443 (1969). <sup>j</sup> E. A. Blom, B. R. Penfold, and W. T. Robinson, *ibid.*, **A**, 913 (1969).

the averaged Sn-Cl bond lengths in octahedral tin complexes with the sum of the steric angles shows that the longest experimental Sn-Cl bond lengths are found in the molecules which have the largest sum of steric angles.

The average Sn-Cl bond lengths, as well as the variations in the apical and equatorial bond lengths in five-coordinate species, may also be correlated with the sum of steric angles. Experimental data are available for two five-coordinate tin species<sup>13,14</sup> which contain both equatorial and apical Sn-Cl bonds, namely, SnCl<sub>5</sub><sup>-</sup> and (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>3</sub><sup>-</sup>. These data are shown in Table VI. It

**Table VI.** Average Sn-Cl Bond Lengths and Sum of Steric Angles for Two Five-Coordinate Tin Complexes

| Complex   | Av bond lengths, Å |        | All bonds | Sum of steric angles, deg |
|---|--------------------|--------|-----------|---------------------------|
|   | Equatorial         | Apical |           |                           |
| SnCl <sub>5</sub> <sup>-</sup> <sup>a</sup>                                 | 2.36               | 2.38   | 2.37      | 485                       |
| (CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>3</sub> <sup>-</sup> <sup>b</sup> | 2.35               | 2.54   | 2.48      | 557                       |

<sup>a</sup> Reference 13. <sup>b</sup> Reference 14.

will be observed that the average Sn-Cl bond length in (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>3</sub><sup>-</sup> is greater than the average Sn-Cl bond length in SnCl<sub>5</sub><sup>-</sup>, a fact which is consistent with the sums of the steric angles derived from covalent radii.

Also, a comparison of the apical and equatorial bond lengths reveals that the apical bond lengths are longer than the equatorial ones, and that upon the replacement of chlorine atoms by the larger methyl groups, the bond length differential between apical and equatorial Sn-Cl bonds increases significantly. These variations are consistent with a nonbonded interaction model, since the nonbonded repulsions of an atom in an apical position are greater than the nonbonded repulsions of an atom in an equatorial position. Thus, the observed differences may be explained, if it is assumed that the repulsive interactions are most effectively reduced by a lengthening of the apical bond. Similar conclusions have also been reached by considering only the electronic properties of the ligands and the central atom.

**Isomeric Configurations in Mononuclear Tin Complexes.** The criterion for predicting which isomer of a complex is most likely to exist in terms of a nonbonded interaction model is that the existing isomeric configuration best avoids steric crowding.

The amount of crowding in cis- and trans-octahedral configurations, for example, may be estimated by summing the steric angles (for each configuration) in the three planes which contain four donor atoms and the central atom. Then, the isomer which has the greatest sum of steric angles in a particular plane may be assumed to correspondingly have the greatest nonbonded repulsive interactions, and will *not* be the isomer which is predicted. This especially applies when the van der Waals spheres of the donor atoms overlap in a particular configuration, since the forces between nonbonded atoms will then be strongly repulsive and very sensitive to small changes in nonbonded interatomic distances. Considering the arrangement of four chlorine atoms and two oxygen atoms in both the cis and trans configurations of an SnCl<sub>4</sub>·2L complex, one obtains the

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(12) Y. M. Chow, *Inorg. Chem.*, **9**, 794 (1970).

(13) R. F. Bryan, *J. Amer. Chem. Soc.*, **86**, 733 (1964).

(14) F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968).

following sums for the steric angles which lie in the three mutually perpendicular planes that describe the octahedral geometry: cis 374, 374, and 358°; trans 389, 358, and 358°. It can be seen that the trans configuration has a plane which contains a greater amount of overlap between adjacent van der Waals surfaces than the overlap found in any of the three planes which describe the cis configuration. In addition to avoiding close contacts by virtue of the *arrangement* of donor atoms, the cis configuration may further reduce nonbonded interactions by a *distortion* of the octahedral bond angles.<sup>15</sup> Consequently, the cis configuration is the preferred geometry for these complexes.

The existence of cis-trans isomers in  $\text{SnCl}_4 \cdot 2\text{L}$  complexes has been discussed previously from the point of view of both steric effects and  $d\pi-p\pi$  bonding.<sup>16</sup> No distinction was made in that work, however, between a large ligand atom and a large sterically hindered ligand. In the present interpretation, some significance is placed upon this distinction.

Let a bulky or sterically hindered ligand be considered as a ligand which has atoms beyond the donor coordination sphere that lie outside the steric angle. If two such ligands were to occupy a cis configuration in the coordination sphere, strong repulsive interactions would exist between the adjacent ligand atoms that lie outside the steric angle. These repulsions could be reduced by a widening of the angle between the two bulky ligands; however, this would also crowd the donor atoms of the other ligands into a smaller portion of the coordination sphere. If, instead, these large ligands assume a trans relationship, then the nonbonded interaction between them will be negligible, but, just as importantly, the donor atoms of the small ligands may pack efficiently between the large ligands, and the total nonbonded repulsions will be lessened. Thus, ligands such as pyridine, trimethylamine, ethyl ether, and diethyl sulfide, which have small donor atoms but are nevertheless bulky, occupy trans positions in  $\text{SnCl}_4 \cdot 2\text{L}$  complexes.<sup>17-19</sup>

A large monatomic ligand atom, on the other hand, is located in the coordination sphere of the donor atoms, and its nonbonded interactions or van der Waals contacts are exerted directly against adjacent donor atoms. Consequently, the relative positions of large ligand atoms in the coordination sphere will depend upon the size and position of the other donor atoms in the coordination sphere, and a configuration will be achieved which minimizes their nonbonded interactions. This is invariably achieved by the cis configuration.

It should be mentioned that for octahedral structures of the form  $\text{MA}_3\text{B}_3$ , where A and B are monatomic ligands with substantially different steric angles, the cis configuration minimizes nonbonded repulsions, regardless of whether the A or B atoms are larger. The steric preference of four large ligands for a cis-octahe-

dral configuration is readily apparent.<sup>16</sup> That such may also be the case when there are only two large ligands is not quite so obvious. This may again be understood in terms of the three perpendicular planes through the central atom. If two large donor atoms occupy trans positions, there will be two planes which contain the two large ligands, and thus have large nonbonded interactions. In the cis configuration there will be only one such plane, and when the ligands achieve the optimum distorted configuration, the nonbonded repulsions will be the same as those in a trans plane with two large ligands. Since the cis configuration has only one crowded plane, its nonbonded repulsions should be slightly less. Thus, with this line of reasoning, all the mixed-halohalo complexes of tin with the  $\text{MA}_3\text{B}_3$  formulation would be expected to have a cis configuration. It has been reported that most and possibly all of the mixed-halo species,  $\text{SnCl}_4 \cdot \text{Br}_2^{2-}$ ,  $\text{SnCl}_4 \cdot \text{I}_2^{2-}$ ,  $\text{SnCl}_2 \cdot \text{Br}_4^{2-}$ ,  $\text{SnCl}_2 \cdot \text{I}_4^{2-}$ ,  $\text{SnBr}_4 \cdot \text{I}_2^{2-}$ , and  $\text{SnBr}_2 \cdot \text{I}_4^{2-}$ , have the cis-octahedral configuration.<sup>20</sup> This observation is consistent with the simple steric interpretation presented here. By the same argument, the *facial* geometry should be preferred for  $\text{A}_3\text{B}_3$  molecules, where A and B are monatomic ligands with substantial differences in their steric requirements.

The prediction of the existing isomer for octahedral dimethyltin complexes fails when based solely upon the nonbonded interaction criterion. This failure may be due to the electronic stability of the linear  $(\text{CH}_3)_2\text{Sn}^{2+}$  moiety,<sup>21</sup> a species which is known to commonly occur in solution. This suggests that the predictiveness of this approach may be restricted to structures in which there are similar amounts of ionic character in the central atom-donor atom bonds. Given that the steric conditions around the central tin atom are not drastic enough to substantially alter the linear relationship of the methyl groups, the arrangement in octahedral dimethyltin complexes may be thought of as constructed from the placement of equatorial ligands around the linear  $(\text{CH}_3)_2\text{Sn}^{2+}$  ion. Thus, the observed trans methyl, cis chlorine, cis oxygen configuration<sup>22</sup> for  $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2(\text{CH}_3)_2\text{SO}$  represents a geometry which reduces nonbonded interactions through molecular distortions, while still preserving the trans relationship of the two methyl groups on the central tin atom.

The dimethyltin complex  $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2(\text{pyridine } N\text{-oxide})$ , has a trans,trans,trans configuration.<sup>23</sup> This arrangement of ligands may also be understood by considering the molecule as a complex of the linear dimethyltin moiety. Then, the placement of two pyridine *N*-oxide ligands and two chlorine atoms into trans positions in the equatorial plane is necessary to avoid an unfavorable steric interaction between the bulky pyridine *N*-oxide ligands.

The steric criterion may also be applied to the isomeric configurations of five-coordinate molecules, in which case the isomer that exists may be predicted

(15) The larger nonbonded repulsions in a trans structure may be reduced only by an increase in central atom-donor atom bond lengths, a process which usually requires considerable energy, or by a lowering of the symmetry through an out-of-plane puckering of the four chlorine atoms, which would still require some bond lengthening. It may be possible to observe such a puckering effect in  $\text{SnCl}_4 \cdot 2\text{L}$  complexes which have the trans-octahedral configuration.

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

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(18) T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967).

(19) T. Tanaka and T. Kamitani, *ibid.*, **2**, 175 (1968).

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(21) (a) R. S. Tobias, *Trans. N. Y. Acad. Sci., Ser. II*, **31**, 913 (1969); (b) I. R. Beattie, *Quart. Rev., Chem. Soc.*, **17**, 382 (1963); (c) M. M. McGrady and R. S. Tobias, *J. Amer. Chem. Soc.*, **87**, 1909 (1965).

(22) N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1257 (1970).

(23) E. A. Blom, B. R. Penfold, and W. T. Robinson, *ibid.*, **A**, 913 (1969).

by the corollary that ligands which occupy apical positions have the smallest steric angles. Stated in this way, this generalization also incorporates the observed differences in the lengths of apical and equatorial bonds to the same type of ligand.

This corollary concerning the stereochemistry of five-coordinate species has an analogous statement based on the electronic point of view,<sup>24</sup> namely that in a trigonal-bipyramidal structure, the most electronegative ligands assume an apical position. Probable exceptions to both this observation and the corresponding steric statement are  $(CF_3)_2PF_5$  and  $(C_2F_5)_2PF_5$ .<sup>24</sup> It is interesting to note, however, that the plausible explanation of why these molecules do not follow the rule, which is that the fluoroalkyl-fluoroalkyl repulsion is so large that the fluoroalkyl ligands occupy apical positions, is steric in nature. Thus, the bulky CF groups occupy apical (trans) positions, which apparently allows the nonbonded repulsions outside the donor coordination sphere to be minimized.

**Comparison with the Valence Shell Electron Pair Repulsion (VSEPR) Model.** The stereochemical model presented in this paper predicts the shape of molecules in terms of the atom-atom repulsions around a central atom. Starting with a different set of basic assumptions, however, the highly successful VSEPR model developed by Gillespie and Nyholm<sup>25</sup> also aims at predicting the arrangement of atoms around a central atom by distributing the valence shell electron pairs of the central atom such that their repulsions are minimized. Each model disregards the factors upon which the other is based, but this does not mean that the two models are necessarily mutually exclusive. Whether it is assumed that molecular shape is determined solely by atom-atom repulsions or by the repulsion of electron pairs, a serious approximation has been made, since *both* types of interactions exist in molecules. Therefore, it is informative to delineate the conditions under which a particular model is most applicable.

When the number of bonded atoms and the number of valence electron pairs of the central atom are not equal, that is to say, when there are lone pairs in the valence shell, the two models necessarily predict different geometries. The criterion for determining which model will best apply to a particular molecule is the relative magnitudes of the repulsive van der Waals interactions between ligand atoms and the repulsive Pauli forces between electron pairs.<sup>26</sup> If a lone pair of electrons exists at the central atom when there are

less than six donor atoms in the coordination sphere, the separation between donor atoms is usually greater than the van der Waals separation, and the shape of the molecule is most strongly influenced by the electron pair repulsions of the central atom. If there are six or more donor atoms in the coordination sphere, the distance between donor atoms may be approximately equal to or shorter than the van der Waals separation, in which case the repulsive nonbonded interactions are generally greater than the repulsive forces between the electron pairs, and the molecular geometry is governed by the nonbonded interactions. Thus, the regular octahedral shapes<sup>27</sup> of  $SbBr_6^{3-}$ ,  $TeCl_6^{3-}$ , and  $TeBr_6^{3-}$ , in which the central atom has seven electron pairs, may be attributed to the large repulsive interactions between the halogen atoms in the coordination sphere.

When the number of bonded atoms and the number of valence shell electron pairs are identical, the two models give very similar results, because the molecular shapes are then constructed with the same symmetry arguments. In these cases, the use of the nonbonded interaction model may be preferable, since this approach gives quantitative or semiquantitative estimates of the deviations to be expected from idealized geometries, especially in molecular environments where the separations between ligands are close to the van der Waals distance.

### Summary

The model has been applied to several monodentate mononuclear complexes of tin that exhibit a variety of coordination numbers and distorted polyhedral shapes. The agreement between experimental results and those calculated from the model emphasizes the influence that nonbonded interactions have on the geometry of tin complexes and indicates that intramolecular steric effects should be evaluated before the geometry of molecules is attributed solely to the electronic properties of the central and donor atoms. The predictive ability of the model suggests that the approach may be generally applicable to molecules in which the separations between donor atoms approximate the normal van der Waals distances. The model may possibly be refined by employing a more direct solution to the three-dimensional distribution of donor atoms, or extended by modifying the procedure to include chelate structures.

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