Journal of Organometallic Chemistry, 107 (1976) 49—54

THE STRUCTURE OF DIMETHYLTIN COMPLEXES

D.L. KEPERT
School of Chemistry, The University of Western Australia, Nedlands, Western Australia, 6009 (Australia)

(Received September 8th, 1975)

Summary

It is shown that the new type of six-coordinate stereochemistry found in $[Sn(NO_3)_2Me_2]$, $[Sn(S_2CNMe_2)_2Me_2]$, and $[Sn\{ON(Me)C(Me)O\}_2Me_2]$, is that which is predicted from simple ligand—ligand repulsion energy calculations.

Introduction

Recent X-ray structural determinations on $[Sn(NO_3)_2Me_2]$ [1], $[Sn(S_2CNMe_2)_2Me_2]$ [2], and $[Sn\{ON(Me)C(Me)O\}_2Me_2]$ [3] have demonstrated the existence of a new type of six-coordinate stereochemistry. Two coordination sites are occupied by methyl groups, and the other four by the two bidentate ligands. This new stereochemistry may be regarded as a gross distortion of the more usual *trans*-octahedral stereochemistry as indicated in Fig. 1. The distortions observed may be summarised:

(i) The two bidentate ligands swivel towards each other, so that the angle between the lines joining the tin atom to the midpoints of the bidentate ligands is decreased from 180° to ~120°. The bidentate ligands remain coplanar with the metal atom.

(ii) Each bidentate ligand becomes grossly asymmetric, one tin—ligand bond length being ~20% greater than the other. These two longer bonds are *cis* to each other.

The detailed stereochemistries of the bidentate ligands about the tin atoms are shown in Fig. 2, which also includes *trans*-$[Sn(MeCOCHCOMe)_2Me_2]$ for comparison [4].

(iii) The C—Sn—C angle is reduced from 180° to ~140° (143.6° in $[Sn(NO_3)_2Me_2]$, 136° in $[Sn(S_2CNMe_2)_2Me_2]$, and 145.8° in $[Sn\{ON(Me)C(Me)O\}_2Me_2]$). The C—Sn—C plane and the Sn(bidentate)$_2$ plane remain at right angles to each other, the complexes retaining C_{2v} symmetry.

On the other hand the closely related compounds $[Sn(MeCOCHCOMe)_2$-

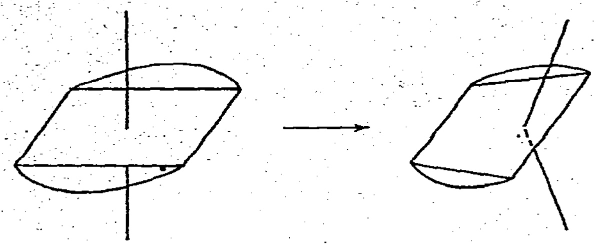

Fig. 1. Distortion of *trans*-octahedral stereochemistry to skew-trapezoidal bipyramidal stereochemistry.

Me_2] and [$SnCl_2(C_5H_5NO)_2Me_2$] [5] have normal octahedral structures, with C—Sn—C angles of 180.0°.

The creation of these "skew-trapezoidal bipyramidal" structures has been attributed to an octahedron distorted by the (unstated and unobvious) steric demands of the *N*-methyl-*N*-acetylhydroxylaminato ligand [3], to a very flattened tetrahedron with each nitrate group imagined as a unidentate ligand [1] (taking the "centre of gravity" of the nitrate group as the tin—nitrogen vector the relevant angles are N—Sn—N 131°, C—Sn—C 144°), and to a very distorted tetrahedron with each dithiocarbamate ligand considered as bonding only through the more closely bonded sulphur atom [2] (S—Sn—S 136°, C—Sn—C 83°). It should be emphasised that treating each bidentate ligand merely as a unidentate ligand does not assist in the understanding of the orientation of both potential donor atoms about the tin atom.

It is the purpose of this work to show that the three distortions observed above are precisely those expected from considerations of ligand—ligand repulsion energy.

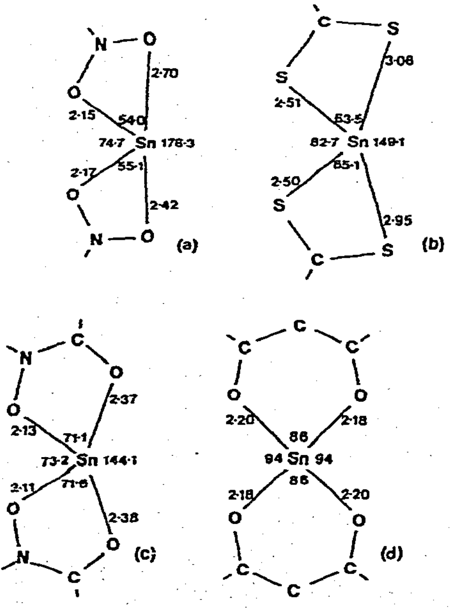

Fig. 2. Trapezoidal Sn(bidentate)$_2$ planes in (a) [$Sn(NO_3)_2Me_2$], (b) [$Sn(S_2CNMe_2)_2Me_2$], (c) [Sn{ON(Me)C(Me)O}$_2Me_2$], (d) [$Sn(MeCOCHCOMe)_2Me_2$].

Calculations

The stereochemical arrangement of any number of ligand donor atoms surrounding a central metal atom may be calculated by minimisation of the total repulsion energy U, obtained by summing over all donor atom-donor atom repulsions (or alternatively the equivalent valence-shell electron pair repulsions). It is assumed that the repulsive energy u_{ij} between any two donor atoms i and j (or alternatively, between any two electron pairs i and j) is proportional to some inverse power n of the distance d_{ij} between them. If all bond lengths are equal, that is all donor atoms lie on the surface of a sphere of radius unity, then the results can be expressed in the form 1, where a_n is the proportionality

$$U = \sum_{ij} u_{ij} = \sum_{ij} a_n \, d_{ij}^{-n} = a_n X \qquad (j > i) \tag{1}$$

constant and X the repulsion energy coefficient which is a function of n and the geometry of the coordination polyhedron. The total repulsion energy U can also be divided into the repulsions V_i experienced by each of the donor atoms, by dividing the repulsion between any pair of donor atoms equally between them as given in eq. 2, where Y_i are the individual atom repulsion

$$V_i = \sum_{i} u_{ij}/2 = a_n Y_i \tag{2}$$

energy coefficients. The most appropriate value of the power n cannot be known exactly, the best fit with experiment usually being obtained for $n \sim 6$. Fortunately the conclusions obtained are not very dependent upon the assumed value of n. In this work the previous custom of using values of 1 (for a purely Coulombic interaction), 6, and 12 is continued.

The location of each donor atom about the central atom is given by its spherical coordinates ϕ_i and θ_i. In contrast to earlier work [6], no assumed symmetry was imposed on the arrangement of donor atoms.

It is assumed that each bonded bidentate ligand is sufficiently rigid that interaction between its donor atoms can be considered to be constant, and can therefore be neglected when comparing otherwise different stereochemistries. The repulsion energy was calculated as a function of the "normalised bite" b of the bidentate ligands, which is defined as the distance between the two donor atoms of the same ligand.

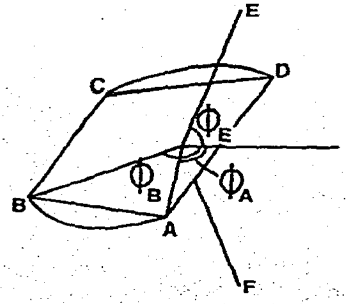

Fig. 3. General stereochemistry for $[M(bidentate)_2(unidentate)_2]$.

For large values of the normalised bite, $b \sim 1.2$—1.5, two minima are found on each potential energy surface, corresponding to the usual *cis*- and *trans*-octahedral isomers of [M(bidentate)$_2$(unidentate)$_2$]. Only the latter is relevant to this work. In all cases it is found that the stereochemistry corresponding to this minimum possesses C_{2v} symmetry, and is completely defined by ϕ_A, ϕ_B, and ϕ_E, the angles the metal—ligand bonds make to the two-fold axis (Fig. 3). Moreover ϕ_A and ϕ_B are related to b by eq. 3.

$$b = 2\sin((\phi_B - \phi_A)/2) \qquad (3)$$

Results and discussion

The angular parameters corresponding to the stereochemistry of minimum repulsion energy are shown in Fig. 4. Bidentate ligands which have relatively large normalised bites ($b \sim 1.2$—1.5) are expected to form the undistorted *trans*-octahedral structure with $\phi_A + \phi_B = 180.0°$, $\phi_E = 90.0°$. This is in agreement with the structure of [Sn(MeCOCHCOMe)$_2$Me$_2$].

As the normalised bite is decreased however, it is predicted that both ϕ_A and ϕ_B will increase (Fig. 4), converting the rectangle formed by the two bidentate ligands into a trapezium. The metal—unidentate ligand bond is simultaneously skewed away from the normal to this plane, decreasing ϕ_E and the angle between the two metal—unidentate ligand bonds. At very low values of the normalised bite, this stereochemistry does not exist as a discrete minimum, the only minimum on the potential energy surface being that of the distorted

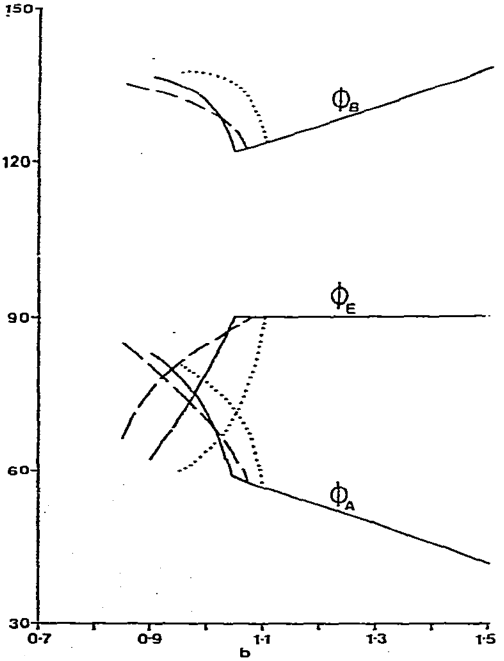

Fig. 4. Angular parameters, in degrees, as a function of normalised ligand bite b: dotted line, $n = 1$; full line, $n = 6$; broken line, $n = 12$.

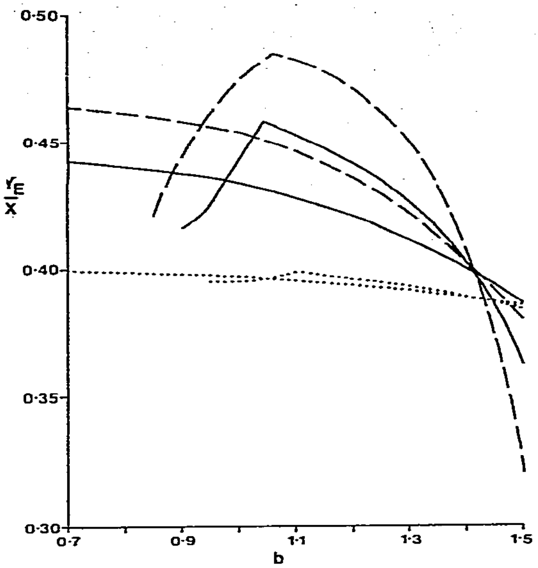

Fig. 5. Contribution of the unidentate ligands towards the total repulsion energy, Y_E/X, as a function of normalised bite b: dotted lines, $n = 1$; full lines, $n = 6$; broken lines, $n = 12$. The discontinuous lines correspond to the *trans*-octahedral-skew-trapezoidal bipyramidal structures. The curves extending over the full range of b correspond to the *cis*-octahedral structure.

cis-octahedral structure. The extent of the lines in Fig. 4 indicates the range of stability of this stereochemistry. The precise angles predicted should not be regarded as very meaningful because of the chemical differences between the unidentate and bidentate ligands, and because of the asymmetry of the bidentate ligands (see below).

A simple reason for this distortion of the *trans*-octahedral structure to the skew-trapezoidal bipyramidal structure is not self-evident. Fig. 5 shows the contribution made by the unidentate ligands towards the total repulsion energy, Y_E/X, as a function of normalised bite b. For *trans*-octahedral complexes the repulsion energy coefficient Y_E associated with the unidentate ligands is not a function of the normalised bite, since the distance between unidentate and bidentate donor atoms remains at the constant value of $2^{1/2}$, and the distance between the unidentate ligands remains at the constant value of 2. The repulsion energy coefficient between the bidentate ligands however decreases rapidly as the normalised bite is decreased, and the rectangular plane becomes increasingly elongated. The repulsion energy experienced by the unidentate ligands relative to the total repulsion energy therefore increases rapidly as the normalised bite is decreased, for example much more rapidly than is observed in *cis*-[M(bidentate)$_2$(unidentate)$_2$] complexes (Fig. 5). The distortion of the *trans*-octahedral structure to the skew-trapezoidal bipyramidal structure removes this imbalance (Fig. 5).

Repulsion energy calculations show that as the metal—unidentate ligand bond length decreases relative to the metal—bidentate ligand bond length, the distortion to the skew-trapezoidal bipyramidal structure commences at larger values of b, which is as intuitively expected.

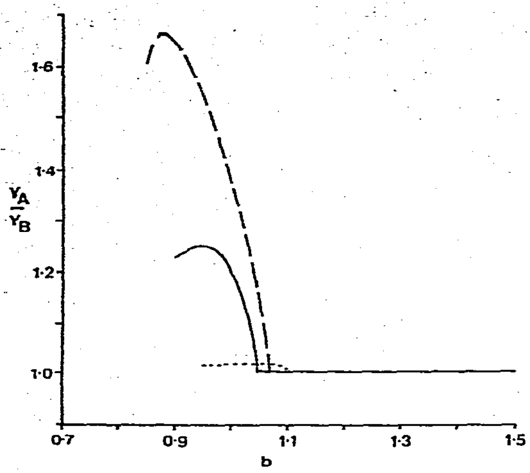

Fig. 6. Ratio of the bidentate ligand repulsion energy coefficients, Y_A/Y_B, as a function of normalised bite b: dotted line, $n = 1$; full line, $n = 6$; broken line, $n = 12$.

The relative repulsion energy Y_A/Y_B associated with the two ends of each bidentate ligand is shown as a function of b in Fig. 6. It can be seen that the A end of the bidentate ligand in the skew-trapezoidal bipyramidal structure experiences considerably greater repulsion than does the B end of the bidentate ligand. This readily accounts for the gross asymmetry observed in the bidentate ligands (Fig. 2). The value of the ratio Y_A/Y_B is more than twice that calculated for *cis*-[M(bidentate)$_2$(unidentate)$_2$].

Repulsion energy calculations show that the extent of this asymmetric distortion of the bidentate ligand increases as the metal-unidentate bond length decreases, which is again as intuitively expected. The skew-trapezoidal bipyramidal structure is also increasingly favoured if asymmetric bidentate ligands such as ON(Me)C(Me)O are used in place of symmetric bidentate groups.

References

1 J. Hilton, E.K. Nunn and S.C. Wallwork, J. Chem. Soc. Dalton Trans., (1973) 173.
2 T. Kimura, N. Yasuoka, N. Kasai and M. Kakudo, Bull. Chem. Soc. Jap., 45 (1972) 1649.
3 P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc. Dalton Trans., (1975) 826.
4 G.A. Miller and E.O. Schlemper, Inorg. Chem., 12 (1973) 677.
5 E.A. Blom, B.R. Penfold and W.T. Robinson, J. Chem. Soc. A, (1969) 913.
6 D.L. Kepert, Inorg. Chem., 12 (1973) 1944.