acteristic "inner filter effect" discussed by Ellis.[5] One characteristic of excimer emission is a quadratic dependence on concentration. The linear dependence found in this work is a further piece of evidence that the 405-nm emission is not that of an excimer.

From the above experiments we conclude that the emission attributed to an acetone monomer by O'Sullivan and Testa is due to an impurity, and that the emission at 405 nm is the true acetone monomer fluorescence. As a result, we conclude that the gas-phase emission of 2-pentanone is most likely due to a monomer species.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation for partial support of this work. Funds from the National Science Foundation and E. I. du Pont de Nemours and Company were used to purchase the spectrofluorometer. Discussions with a number of our colleagues at Hope College are gratefully acknowledged.

(5) E. W. Ellis in "Fluorescence and Phosphorescence Analysis," D. M. Hercules, Ed., Interscience Publishers, New York, N. Y., 1966, Chapter 2.

Gordon D. Renkes, F. Sheldon Wettack
Department of Chemistry, Hope College
Holland, Michigan 49423

Received September 9, 1969

Metal Ion–Aromatic Complexes. IX. The Structure of a Seven-Coordinate Tin(II)–Benzene Complex, $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$

Sir:

In an earlier communication[1] we reported the preparation and characterization of the remarkable and previously unknown compounds $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$, $(C_6H_6)_2 \cdot Pb(AlCl_4)_2$, $C_6H_6 \cdot 2TlAlCl_4$, $(C_6H_6)_2 \cdot TlAlCl_4$, and $C_6H_6 \cdot BiCl_2AlCl_4$. All the available evidence at that time (infrared, Mössbauer, nmr) pointed to a highly symmetrical structure for $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$ (most likely a D_{6h} ferrocene type). To establish unambiguously the molecular stereochemistry of this Sn compound, we undertook the solution of the crystal structure and found an unexpected pentagonal bipyramid seven-coordinate Sn(II).

A diffraction quality single crystal 0.65 × 0.35 × 0.80 mm was coated with Vaseline and sealed in a thin-walled glass capillary. The crystal was mounted with the long direction, [101], approximately parallel to the ϕ axis on the Picker diffractometer, and aligned by well-known methods.[2] A least-squares fit of the χ, ϕ, 2θ, and ω angles of 25 carefully centered reflections[2] gave the crystal parameters with Mo Kα radiation (λ 0.71068 Å): $a = 11.300(2)$, $b = 17.355(8)$, $c = 12.655(6)$ Å, and $\beta = 110.04(1)°$, $P2_1/n$.[3] With $Z = 4$, $\rho_{calcd} = 1.84$ g cm^{-3}, $\rho_{obsd} = 1.76–2.01$ g cm^{-3} in a CCl_4–CBr_3H mixture; μ was calculated to be 26.2 cm^{-1} with Mo Kα. No corrections were made for absorption since there is invariably some decomposition product coating the crystal, and this absorption plus the effect of the capillary and Vaseline collectively probably outweigh simple crystal absorption effects. Peaks were scanned at 1°/min for 144 sec and backgrounds were estimated at ±1.2° 2θ of peak maxima by stationary counting for 40 sec. By this means 3430 independent *hkl* planes were measured for $2\theta < 70°$. The integrated intensity was calculated from $I(\text{net}) = I(\text{scan}) - 1.40(B_1 + B_2)$. The reflections were considered nonzero if $I(\text{net}) > 2.5[1.40(B_1 + B_2)^{1/2}]$. By this criterion 1346 reflections were retained. The structure was solved by conventional heavy atom methods[4] and refined by full matrix least squares[5] with weights determined from intensity statistics and a 4% intensity factor,[6] to a final R of 0.063[7] and weighted R of 0.076.

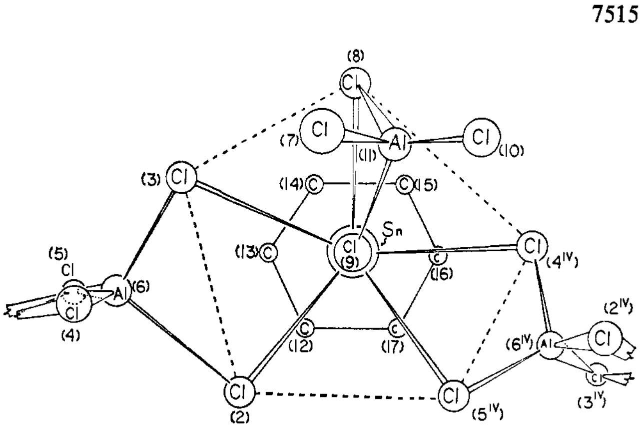

Figure 1. Idealized view of the $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$ complex showing the seven-coordinate pentagonal bipyramidal Sn(II). The view is down the axial Cl which is superposed on the Sn atom. The chain is built up by Cl(4) and Cl(5) bonded to an adjacent Sn(II) to the left, and Cl^{IV}(3) and Cl^{IV}(2) bonded to an adjacent Sn(II) to the right. The dotted lines define the pentagonal plane.

The gross structure features of $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$ may be described by a Sn(II) moiety bonded to two chlorine atoms from each of three different $AlCl_4^-$ ions (sharing of tetrahedral edges with Al), to form a linear chain structure propagating in approximately the [111] direction. The Sn(II) polyhedron is completed by a symmetrical axial coordination to one of the benzene rings that may be considered to be lying on the surface of the chain. The benzene rings of adjacent chains are back to back. However, the second aromatic entity lies in a cleft between chains and should be regarded as a molecule of solvation. This arrangement of $AlCl_4^-$ units and benzene about Sn(II) gives the metal a coordination number of seven in an approximate pentagonal bipyramid geometry. This geometry assumes the benzene fills only one axial coordination site (Figure 1). It is to be noted that Sn(II) is essentially tris-chelated by $AlCl_4^-$ anions.

---

(1) Th. Auel and E. L. Amma, *J. Amer. Chem. Soc.*, **90**, 5941 (1968).

(2) (a) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1967; (b) K. Knox in "Master Card Program for Picker Four-Angle Programmer," Picker Instruments, Cleveland, Ohio, 1967, p 11; (c) W. R. Busing and H. A. Levy, *Acta Cryst.*, **22**, 457 (1967).

(3) "International Tables for X-Ray Crystallography," Vol. 1, N. F. M. Henry and K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1962.

(4) Patterson and electron density calculations performed on an IBM 7040 with ERFR-3 program, a modification of ERFR-2 of Sly–Shoemaker–Van den Hende by D. R. Harris.

(5) Least-squares refinement performed with ORFLS of W. Busing, K. O. Martin, and H. A. Levy (ORNL-TM-305, 1962) with local modifications. Scattering factors and other computer programs used are to be found in M. S. Weininger, J. E. O'Connor, and E. L. Amma, *Inorg. Chem.*, **8**, 424 (1969).

(6) S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957).

(7) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = \{\Sigma\omega[|F_o| - |F_c|]^2\}^{1/2}/[\Sigma\omega F_o^2]^{1/2}$.

The equatorial Sn–Cl distances range from 2.884 (7) to 3.291 (7) Å, and the axial Sn–Cl distance is 2.766 (7) Å. These are somewhat long compared to the covalent radii sum of 2.39 Å,[8] but are real covalent interactions since the sum of the van der Waals radii is 4 Å.[8] The Cl(equatorial)–Sn–Cl(equatorial) angles vary between 73° and 81° with individual esd's of ±0.60° (regular pentagon = 72°). The Sn is displaced 0.6 Å from the least-squares plane defined by the five equatorial halogens toward the benzene ring. We view this displacement as arising from a combination of steric constraints imposed by the chelated $AlCl_4^-$ groups and van der Waals repulsion between C and Cl. The Sn–C distances are not significantly different from the 3.08-Å average, and the Sn to center of ring distance is 2.74 (3) Å. The benzene carbon–carbon distances are indistinguishable from free benzene. The Cl(axial)–Sn–center of benzene ring angle is 180° within experimental error. These metal–carbon distances are also quite long compared to, *e.g.*, ruthenocene[9] [Ru–C = 2.21 (2) Å], but again are much shorter than the 4 Å[8] expected from van der Waals radii. These "long" metal–carbon distances are compatible with our views of the bonding; *vide infra.*

There has been considerable recent activity in higher coordination number metal complexes as demonstrated by a symposium[10] and a review.[11] Most seven-coordinate pentagonal bipyramid complexes (few have been definitely established) involve uranium, zirconium, and molybdenum.[12a] However, Hoard[12b] has reported a pentagonal bipyramid structure for tristropolonotin(IV) chloride and hydroxide. We believe our results are the first report of a pentagonal bipyramid seven-coordinate Sn(II) entity.

The nature of the bonding in this pentagonal bipyramid complex is particularly interesting. A reasonable energy level diagram can be constructed using benzene π orbitals, considering only σ bonds between Cl and Sn, assuming C_{5v} symmetry[13] and with the energy level diagram of dibenzenechromium[14] as a reference. The a_1, e_2, e_1 halogen orbitals would lie approximately halfway between aromatic e_1 and e_2, whereas the 5s Sn(II) a_1 might lie close to aromatic e_2 but considerably below the b_2. The e_1 and a_1 5p orbitals might be about 5–7 eV above the 5s, and the 5d about 7 eV above the 5p.[15] It seems energetically unfavorable to make much use of the 5d. The filled MO's of the pentagonal bipyramid complex would then be, in order of increasing energy: $(a_1)^2(e_1)^4(a_1')^2(e_1')^4(a_1'')^2(e_2)^4(a_1''')^2$. This corresponds to a closed shell configuration with moderate separation between a_1''' and the lowest empty MO of e_2' symmetry which would be principally nonbonding aromatic. The lowest a_1 and e_1 MO's would be mostly aromatic. The e_1', a_1', a_1'', and e_2 MO's would be chiefly chlorine σ in character, with a_1' being the axial interaction. If the 5d Sn(II) orbitals play a significant role in this complex, it would be in the lowering of the energy of e_2 and e_2'. The e_2 lowering would correspond to increasing the bond order of the equatorial Sn–Cl bonds, and e_2' lowering would be equivalent to "back-bonding" from metal to aromatic. It is to be noted that the bonding between Sn and the halogens involves five equatorial bonds but only six bonding electrons $[(e_1')^4$ and $(a_1'')^2]$, and the Sn–Cl bonds are long as expected. Nevertheless, it must be borne in mind that there is some aromatic mixing in these orbitals, but this is probably small. It is gratifying to see that the highest filled level is $(a_1''')^2$, which is mostly metal in character, since the Mössbauer spectrum shows that the 5s orbitals are almost fully occupied.[16] The principal bonding between metal and aromatic is in the a_1 and e_1 levels which involve metal 5s and 5p, and may be viewed as charge transfer of π electrons into the empty 5p orbitals of Sn(II). When viewed in this way the bonding can also be described in terms of Mulliken's charge-transfer theory.[17]

Presumably, $(C_6H_6)Pb(AlCl_4)_2 \cdot C_6H_6$ is similar to the above in both geometry and bonding. The Tl complexes are different in stoichiometry and probably geometry due to the contrasting requirements of the Tl(I) ion.

Acknowledgment. Financial support was received from the National Science Foundation under Grant No. GP-12282.

---

[8] L. Pauling, "Nature of the Chemical Bond," 3rd ed, The Cornell University Press, Ithaca, N. Y., 1960, pp 246, 260.

[9] E. L. Hardgrove and D. H. Templeton, *Acta Cryst.*, 12, 28 (1959).

[10] Symposium on Unusual Coordination Polyhedra, Abstracts, Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[11] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), 21, 109 (1967).

[12] (a) M. Elder, *Inorg. Chem.*, 8, 2103 (1969); (b) J. L. Hoard, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, paper O3.

[13] Obviously the true symmetry of the complex is not C_6 but much lower. However, this difference would not materially affect the arguments.

[14] E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, 128, 1234 (1959).

[15] C. E. Moore, "Atomic Energy Levels," Vol. III, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1958, p 82.

[16] L. Cathey, University of South Carolina, private communication, 1968.

[17] R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

[18] Address all correspondence to this author.

H. Lüth, E. L. Amma[18]
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received September 9, 1969

Mechanistic and Exploratory Organic Photochemistry. XLIX.[1] Excited-State Aromaticity and Energy Localization. The Di-π-methane Rearrangement of Naphthobarrelenes

Sir:

In our recent study of the di-π-methane rearrangement of benzobarrelene (**1**) to form benzosemibullvalene (**2**), we encountered an intriguing preference for vinyl–vinyl bridging over benzo–vinyl bonding.[2] Energetic arguments were advanced to rationalize this selectivity.[2] Our hypothesis suggested that by lowering the triplet excitation energy of the aromatic moiety of the molecule, one might enforce an aromatic–vinyl bridging process.

For this study 2,3-naphthobarrelene (**6**) and 1,2-naphthobarrelene (**7**) were synthesized by reaction of 2,3-naphthyne (**8**) and 1,2-naphthyne (**9**) with benzene.[3]

---

[1] For paper XLVIII of the series see H. E. Zimmerman and S. S. Hixson, *J. Am. Chem. Soc.*, in press.

[2] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, 90, 6096 (1968).

[3] (a) All compounds analyzed properly. (b) Full experimental details are given in our complete paper. (c) Irradiations were mainly with solution filters and a GEAH6 lamp. (d) Deuterations were *ca.*