most stable isomer at both RHF and MP3 levels of approximation. This is misleading, however, since the expected diradical character for this structure may lead to instability of the RHF wave function. To test this possibility an unrestricted Hartree–Fock calculation was carried out by using the 3-21G basis set at the RHF/3-21G geometry. This lowered the energy of the singlet disilacyclobutadiene by about 20.3 kcal/mol. Further refinement of the wave function using the UHF-NO CI procedure, in which a full π space CI is used and a correct spin eigenfunction is obtained, results in an additional 10.5 kcal/mol lowering. Since the CI corrects for more than just the diradical instability, the actual correction is likely to be in the range of 20.3–30.8 kcal/mol. This will still leave the 1,3-butadiene well above the most stable isomers.

The FORS MCSCF results for the 1,3-disilacyclobutadiene are very similar to the UHF-NO CI results. The 12 configuration π space MCSCF energy is some 31.8 kcal/mol below the RHF energy given in Table I and 1 kcal/mol below the UHF-NO CI result. The SCF configuration represents just 82.3% of this MCSCF wave function, so that one might speculate on the accuracy of the RHF geometry. Nonetheless, the amount of correlation recovered still places isomer **13** at the upper end of the stability order.

Conclusions

We have carried out ab initio calculations on strained ring compounds of the $C_2Si_2H_4$ energy surface. The most stable isomers contain silylene groups and only singly bonded silicon atoms. Of these isomers the most stable is 1-silyl-3-sila-1-cyclopropen-3-ylidene (1). Saturated non-silylene can be found on the SCF surface, disilatetrahedrane, and it is very high in energy relative to those isomers containing silylene groups.

3,4-Disilacyclobuta-1,3-diene and 3,4-disilacyclobuta-2,4-diene are not local minima on the surface. They may be differentiated when they are constrained to C_{2V} symmetry, but they decay to the same nonplanar isomer upon relaxation of those symmetry constraints. 2,4-Disilacyclobuta-1,3-diene was found to possess significant diradical character and cannot be adequately described at the RHF level of calculation. While UHF-NO CI or FORS MCSCF calculations give some energy improvement by accounting for the diradical behavior, they do not indicate it will be the favored isomer on the surface.

Acknowledgment. This work was supported by donors of the Petroleum Research Fund, administered by the American Chemical Society. The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged. We have benefited from several helpful discussions with Professor P. Boudjouk.

Registry No. **1**, 88303-66-6; **2**, 88303-67-7; **3**, 88303-68-8; **4**, 88303-69-9; **5**, 88303-70-2; **6**, 88303-71-3; **7**, 88303-72-4; **8**, 88303-73-5; **11**, 88303-74-6; **13**, 88303-75-7.

Intermolecular Forces and Hyperfine Interactions in Cyclic Dibutyltin Compounds

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A number of cyclic dibutyltin distannoxes have been examined by temperature-dependent ^{119}Sn Mössbauer-effect spectroscopy, both as neat solids and as frozen solutions in *n*-butylbenzene, in order to elucidate the structural similarity and lattice dynamical properties of chiral conformers and their racemic mixtures. The systematics of the isomer shift and quadrupole splitting parameters show that the ring-substituted compounds are all isostructural and suggest—together with the systematics of the temperature dependence of the recoil-free fraction as well as solution molecular weight and NMR data reported earlier—that they consist of dimeric species with pentacoordinated metal centers. No difference (within experimental error) could be observed in the lattice dynamical properties of the neat solid pure chiral conformers and their respective racemic mixtures, suggesting that the differences in the intermolecular packing forces are negligible in their effect on the motional behavior of the Mössbauer-active probe atom. The intensity asymmetry of the two components of the quadrupole doublet resonance was observed to be temperature independent in the range $78 \leq T \leq 170$ K, and there is no evidence of motional anisotropy of the metal atom in these solids in this temperature range.

Cyclic butyltin stannoxanes and distannoxanes have found considerable use in the synthesis of stereospecific macrocycles and serve as useful templates in the construction of ring compounds of varying complexity.[1–6] In this context, it is interesting to note that the structure of these organometallic reagents in solution is still a subject of some controversy and that a number of suggestions have been made[7–9] concerning the configuration of the species

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(1) Shanzer, A.; Schochet, N.; Rabinovich, D.; Frolow, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 326.

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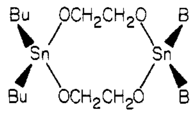
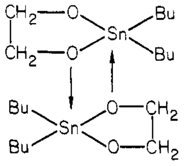
present under reaction conditions as compared to that in the neat solid state.

In an early study, Considine[7] reported that the reaction between Bu_2SnO and ethylene glycol yields a solid product (I, mp 223–226.5 °C) which, on recrystallization from benzene, showed a molecular weight of 586 g mol^{-1} and showed no OH absorptions in the infrared spectrum in $CHCl_3$ or CS_2 solution. From these observations it was inferred that the product was, in fact, a 10-membered heterocycle with a distorted tetrahedral (four-coordinate) environment around the metal atom. Pommier and Valade[10] obtained the proton NMR spectrum of I in dilute cyclohexane or CCl_4 solution and noted that the sharp resonance of the protons on the carbon atom next to the oxygen (3.33 ppm with respect to Me_4Si) was indicative of the same cyclic structure as that suggested by Considine.

Smith et al.,[8] making use of a 60-MHz proton NMR (22.37-MHz ^{119}Sn frequency) spectrometer, observed that the tin resonances in saturated solutions of the cyclic stannoxanes were shifted upfield by 155–189 ppm relative to tetramethyltin and concluded from these data, as well as ^{119}Sn Mössbauer parameters, that the local environment about the metal atom was in fact pentacoordinate. The oxygen-bridged dimeric structure proposed by them is similar to that inferred for the acyclic dimeric dialkoxides [such as $(C_4H_9)_2Sn(OR)_2$, R = CH_3, C_2H_5, etc.] which are liquids at room temperature, on the basis of ^{119}Sn NMR chemical shifts. The two suggested structures can be visualized by representations **a** and **b**, in which the local environments around the metal atom are four- and five-coordinate, respectively.



a



b

Taking advantage of instrumental developments since the earlier studies, Shanzer, Libman, and Gottlieb[5,11] have examined the proton NMR resonances of a number of dibutyltin distannoxanes in deuteriochloroform at room temperature, using high-resolution (270-MHz) methods, and observe two clearly distinguishable chemical shifts for the methyl groups nearest to the chiral centers in monomethyl-substituted racemic and optically active samples. From this observation it was concluded that both the racemic and optically active derivatives form molecular complexes that dissociate into their components on dilution and that their exchange rate is slow ($\tau > 10^{-1}$ s) under the conditions of their experiment. Moreover, the molecular association at high concentrations was presumed to involve an "edge-to-edge" interaction between the two molecular partners that could be exploited in further synthetic steps to give rise to macrocyclic products whose structure is determined by the configuration of the intermediate complex of the starting reagents.

The present study was undertaken to elucidate the following questions concerning the structure, bonding, and solid-state properties of structurally and conformationally related cyclic dibutyltin compounds: (a) Is there a structural similarity in the solid-state conformations of the homologous members of this series? (b) What is the relationship between the structures of these compounds as neat solids and in (frozen, glassy) solutions? (c) Is there an observable difference in the crystal stacking forces between the pure chiral isomer of a particular molecular composition and the racemic mixture of the two conformers? Temperature-dependent ^{119}Sn Mössbauer effect spectroscopy was chosen as the technique likely to be most useful in addressing these questions.

Experimental Section

The subject compounds were synthesized and characterized by methods described earlier.[11] They are all air-stable colorless solids at room temperature and were simply stored in air-tight containers prior to use.

The details of the temperature-dependent ^{119}Sn Mössbauer spectroscopic measurements have been reported earlier.[12–14]

Spectrometer calibration was effected by using the six-line magnetic hyperfine spectrum of metallic iron. The isomer shift reference point was determined from the spectrum of a room-temperature $BaSnO_3$ absorber, using the same source as that employed in the sample measurements. In a typical data set, approximately 10 temperatures were used to determine the thermal dependence of the Mössbauer parameters, and spectrometer calibration was effected before and after each data set. Data reduction was carried out by using a Lorentzian line-shape matrix-inversion least-squares fitting routine, in which line positions, widths, and intensities were allowed to vary as free parameters. The ^{119}Sn Mössbauer source used in these studies was $BaSnO_3$.

In order to ensure that measurements were made on "thin absorbers", we mixed weighed quantities of the neat solid samples with a small amount of an inert carbohydrate[15] and pressed them into self-supporting pellets at a pressure of $\sim 6.9 \times 10^8$ dyn cm^{-2} (10000 lb in^{-2}). These pellets, in turn, were mounted in copper sample holders sandwiched in thin high purity aluminum foil thermal shields and attached to the cold finger end of a controlled-temperature cryostat. Temperature control over the duration of a spectral run at a given temperature (typically 4–8 h) was better than ±0.5 K. Sample thicknesses were typically in the range $(0.3\text{–}3.1) \times 10^{18}$ $^{119}Sn/cm^2$. Frozen solution concentrations were typically 0.04–0.06 M. The frozen solution studies were carried out on solutions of the sample compounds in *n*-butylbenzene, injected into a copper cell fitted with thin glass windows, which was mounted (together with a Pd critical X-ray absorber) in the cryostat, as above, and cooled to liquid-nitrogen temperature before evacuation.

The line widths observed in the Mössbauer spectra were typically in the range 0.85–0.95 mm s^{-1}, and there were no systematic differences noted in the line widths of the high-velocity and low-velocity components of the quadrupole doublet. Moreover, the line widths were found to be temperature independent, indicative of the validity of the "thin absorber approximation" to determine the high-temperature limiting slopes of the ^{119}Sn recoil-free fractions. Typically, for a sample thickness of 1.3×10^{18} ^{119}Sn nuclei cm^{-2}, the optical thickness, *t*, is found to be ~ 0.3 from the observed lattice temperature, using the atomic mass of Sn, and thus no saturation effect corrections have been applied in the subsequent data analysis.

Mössbauer spectra of frozen solution samples of I and VIII were obtained by using *n*-butylbenzene as a solvent. The advantage of this solvent is that the viscosity—and hence the mean-free diffusion path length—varies by many orders of magnitude between room temperature and liquid-nitrogen temperature (the extrapolated viscosity at 77.5 K is 3.5×10^{43} P), and hence it may be assumed that on rapid cooling the solute is trapped in a glassy

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(14) Molloy, K. C.; Bigwood, M. P.; Herber, R. H.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 3709.

(15) Commercial nondairy coffee lightener containing primarily corn solids and hydrogenated vegetable oils to give a dry easily compressible powder.

Table I. ^{119}Sn Mössbauer Data for the Cyclic Dibutyltin(IV) Compounds Discussed in the Text[a]

compd	R_1	R_2	conf[b]	MW(calcd for monomer), g mol^{-1}	^{119}Sn, cm^{-2} × 10^{18}	IS (78 K),[c] mm s^{-1}	QS (78 K),[d] mm s^{-1}	$-d[\ln A(T)/A(78)]/dt$, K^{-1} × 10^{-2}	cc^2 [e]
I	H	H	...	293	3.13	1.212	2.931	1.810	0.982
I	(0.06 M in BuBz)					1.223	3.002	(Γ = 0.938 ± 0.041 mm s^{-1})	
III	CH_3	H	rac	307	1.43	1.144	2.747	1.681	0.990
V	CH_3	H	*R*	307	0.89	1.166	2.829	1.712	0.990
IV	CH_3	CH_3	rac	321	1.31	1.257	3.084	1.406	0.998
II	CH_3	CH_3	*R,R*	321	0.29	1.251	3.058	1.280	0.991
IX	$(CH_3)_2$	H	...	321	0.60	1.144	2.627	1.346	0.994
VIII	CO_2Et	CO_2Et	rac	437	1.14	1.302	3.200	1.011	0.979
VIII	(0.05 M in BuBz)					1.290	3.143	(Γ = 0.974 ± 0.011 mm s^{-1})	0.993
VI	CO_2Et	CO_2Et	*S,S*	437	0.83	1.308	3.182	1.205	0.993
VII	$Bu_2SnOCH_2CH_2S$			309	0.98	1.350	2.899	1.320	0.995

[a] All isomer shift data are with reference to a $BaSnO_3$ spectrum at 295 ± 2 K, obtained using the same Mössbauer source. Line widths (fwhm) for the solids were observed to be 0.85–0.95 mm s^{-1}. The observed line widths for the frozen solution samples are indicated in the table. [b] Conformation around chiral center(s): rac = racemic mixture. [c] With respect to $BaSnO_3$ at 295 ± 3 K; ±0.008 mm s^{-1}. [d] ±0.010 mm s^{-1}. [e] (linear regression correlation coefficient)^2 of ln [$A(T)$] data.

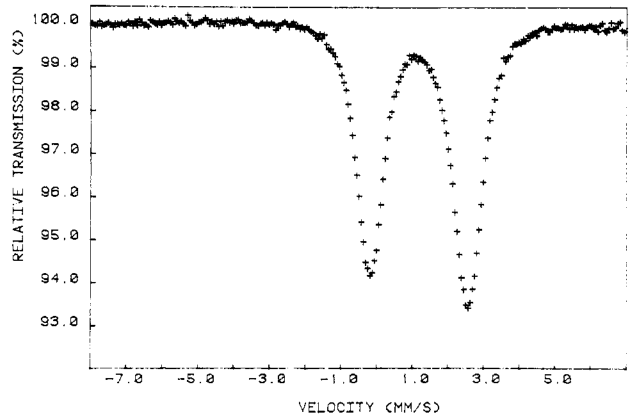

Figure 1. Mössbauer spectrum of I at 80 K. The isomer shift scale is with respect to the resonance maximum of a standard $BaSnO_3$ absorber at 295 K.

matrix rather than forming neat solid crystallites around nucleation centers. The parameters extracted from such spectra are assumed to be those pertaining to isolated solute species.

Infrared spectra of VI were obtained on ~0.5% by weight samples in KBr, using a Perkin-Elmer Model 283 double-beam dispersive spectrometer in the slow scan mode.

Results and Discussion

All of the ^{119}Sn Mössbauer spectra of the subject cyclic dibutyltin stannoxanes examined in the present study consist of a pair of well-separated resonance maxima that are the components of a quadrupole doublet. A typical spectrum is shown in Figure 1, and the numerical data pertaining to the isomer shift (IS) and quadrupole splitting (QS) hyperfine interaction parameters are summarized in Table I.

The isomer shifts are typical of those associated with organotin(IV) compounds[16] and are generally in satisfactory agreement with those which have been reported in the literature.[8] Comparison of the isomer shift value for I observed for the neat solid sample and that observed for the frozen solution of I in *n*-BuBz leads to the conclusion that the bonding environment around the metal atom is essentially the same in both cases. A similar inference appears justified on the basis of the comparison of the neat solid and solution data for VIII, as well as of the isomer shift and quadrupole splitting systematics (vide infra) of all of the compounds examined in the present study. On the basis of isomer shift and quadrupole splitting systematics, it may thus be concluded that the local environment around the metal atom in the dibutyl cyclic stannoxanes is that of a fived-coordinated metal center, with one of the two oxygen atoms in each ring providing a dative coordinate bond to form a dimeric entity in both the solid and solution states. The involvement of a single oxygen atom of each ring in this association is, moreover, consistent with the Mössbauer data for the 2,2-dimethyl member of the series (IX) in which steric hindrance favors bonding by the oxygen bonded to the C3 carbon atom, as well as by the data for the monothiol (VII), in which the *intermolecular* association is again postulated to involve a lone pair of electrons on the oxygen atom of the ring in each monomeric unit. As will be discussed below, the propensity to form dimeric units of similar structure is also reflected in the temperature dependence of the ^{119}Sn recoil-free fraction as observed in the Mössbauer studies on these covalent crystalline solids.

Turning next to the QS hyperfine interaction, it is to be noted from the data summarized in Table I that this parameter spans a rather narrow range (2.6–3.1 mm s^{-1} at 78 K), again consistent with the near constancy of the bonding geometry around the metal atom. Starting with an idealized five-coordinate Sn atom, the bond hybridization is assumed to be sp^{3}d. The five bonds become distinguishable on the basis of the principle embodied in Bent's rule;[17] that is, the tin–oxygen bonds will have a greater share of p character, while two tin–carbon bonds will have a greater share of s character, than is predicted from simple electron counting (five identical bonds each with 20% s character). In addition, in each of the cyclic stannoxanes examined, the oxygen–tin–oxygen bond angle is largely determined by the size of the five-membered ring system. Thus, the final nearest geometry that governs the electric field gradient tensor at the metal atom lattice site is that of a distorted trigonal-bipyramidal structure. Because of the steric requirements of the five-membered ring, the local bonding symmetry around the metal atom will

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(17) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616; *J. Chem. Phys.* **1960**, *33*, 1258; *Chem. Rev.* **1961**, *61*, 275. See also the discussion in: Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1972; p 132 ff.

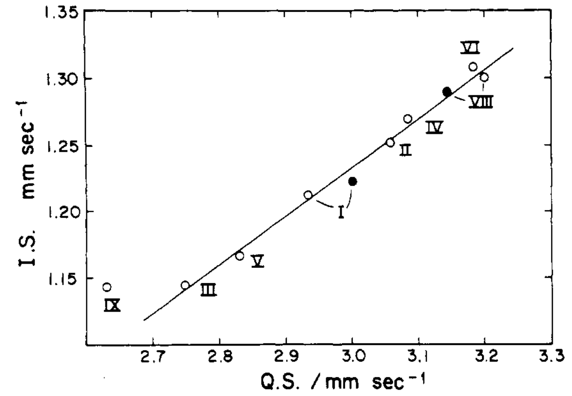

Figure 2. Quadrupole splitting–isomer shift correlation for the dibutyltin stannoxanes discussed in the text. The filled circles for I and VIII refer to frozen glassy solutions in *n*-butylbenzene for these two compounds. All data pertain to measurements at liquid-nitrogen temperature. The straight line represents a linear regression to the data for the neat solids and has a slope of 0.3632 with a correlation coefficient of 0.9960 for the seven data points.

show a significant departure from the idealized sp^3d geometry, and the highest possible *local* symmetry through the Sn atom is likely to be a mirror plane.

Since the overlap between the tin atom sp^3d orbitals and the oxygen atom sp orbitals will be reflected in both the IS parameter (which reflects the s electron density at the metal atom nucleus) and the QS parameter (which reflects both the electron density in the Sn–O bond and the details of the O–Sn–O bond angle), it is not surprising that these two parameters correlate with each other. This correlation is summarized graphically in Figure 2, in which it is noted that an increase in the QS parameter is reflected in an increase in the IS parameter; that is, the greater the departure from an ideal symmetric charge distribution around the metal atom, the greater is the s electron density at the ^{119}Sn nucleus, reflecting the greater s character of the carbon–tin bond.

The differences between the racemic mixtures and the pure conformational isomers in the case of the III, V and II, IV pairs are probably within the experimental errors of the IS and QS parameters at 78 K and are not considered to be significant in the context of the present discussion. In the same light, the near identity in position on the IS–QS correlation diagram of Figure 2 of the neat solid (open data points) and *n*-BuBz frozen solution data (filled data points) for the two cases examined (I and VIII) is consistent with the inference, drawn above, that the local architecture around the metal atom is essentially the same in the neat solid and in the frozen (glassy) solution configurations. It is not clear why the data point for IX, the 2,2-dimethyl cyclic homologue of II and IV, does not fall on the linear regression for the other compounds, and further examples of 2,2-dialkyl-substituted compounds may have to be examined before this apparent anomaly can be clarified.

Turning next to the temperature dependence of the recoil-free fraction [$f(T)$] for ^{119}Sn in these compounds, the simplest phenomenological description of these solids is one in which the *intermolecular* forces are assumed to be much weaker than the *intramolecular* forces and hence that it is possible to envision these molecular solids as consisting of point masses having the effective vibrating mass corresponding to the molecular weight (formula weight) of the respective dimers.[12,18] On the other hand, for solids with nearly equal monomer formula weights, it is possible to distinguish those with strong intermolecular bonding interactions (oligomers or polymers) from those which are essentially monomeric in the solid, by reference to $f(T)$, since the former will have a distinctly smaller value of the slope of ln $f(T)$ vs. temperature, than the latter.

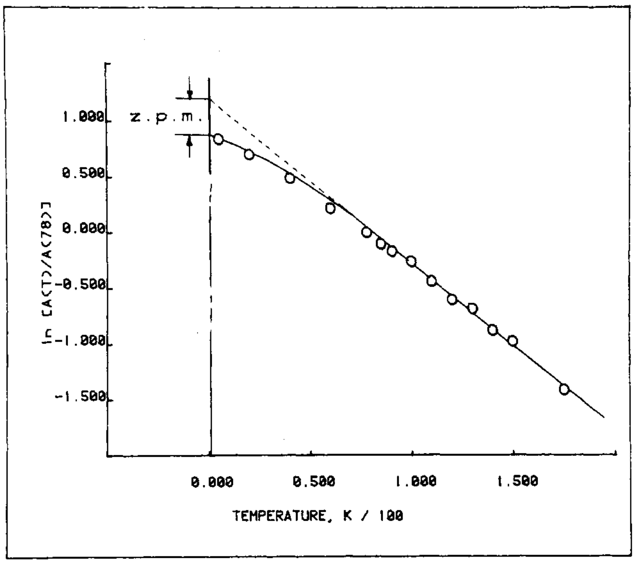

Figure 3. Temperature dependence of the area under resonance curve (normalized to the 78 K datum) for IV. In the thin absorber approximation the slope in the high-temperature limit is equivalent to the temperature dependence of the recoil-free fraction for ^{119}Sn and can be related to the lattice temperature of the solid. The zero-point motion effect (ZPM) is indicatedd in the low-temperature limit.

For all of the subject compounds examined in the present study, the temperature dependence of ln $f(T)$ is a linear function over a sufficiently large interval to permit a reasonably accurate value of this parameter to be determined in the high-temperature limit. A typical data set is shown in Figure 3 for IV, for which the slope of the logarithm of the area (normalized to the 78 K datum) over the interval $60 \leq T \leq 175$ (11 data points) is -1.406×10^{-2} K^{-1} with a correlation coefficient of better than 0.999. The departure from linearity of this regression at low temperatures reflects the zero-point motion of the probe atom (^{119}Sn) in the low-temperature limit.

The temperature dependence of the recoil-free fraction for all of the subject compounds is summarized in Table I and falls in the range $1.28 \times 10^{-2} \leq d \ln f(T)/dT \leq 1.81 \times 10^{-2}$ K^{-1}. The correlation between these slopes and the corresponding monomer molecular weights is shown in Figure 4 from which it is seen that—in consonance with the â priori expectations of the effective vibrating mass model[18]—there is a reasonable linear regression of these two parameters, with the higher molecular weight monomers showing the shallower slopes.

Comparison of the ln $f(T)$ data for the pure conformational isomers and the racemic mixtures (e.g., III and V or II and IV) shows that within the experimental errors of these measurements, the temperature dependencies of the recoil-free fractions are identical for the two kinds of samples. This (near) identity of $d[\ln f(T)]/dT$ for the two cases is again in agreement with the assumption inherent in the model discussed above; that is, that the *intermolecular* forces between dimeric units are much weaker than the *intramolecular* forces which hold the metal atom in the molecule by the nearest-neighbor bonding forces in the (distorted) pentacoordinate environment. Thus, the stacking forces that bind the covalent molecules into the solid are insensitive (in terms of the ^{119}Sn Mössbauer probe) to the intermolecular interaction differences be-

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[18] Rein, A. J.; Herber, R. H. *J. Chem. Phys.* **1975**, *63*, 1021.

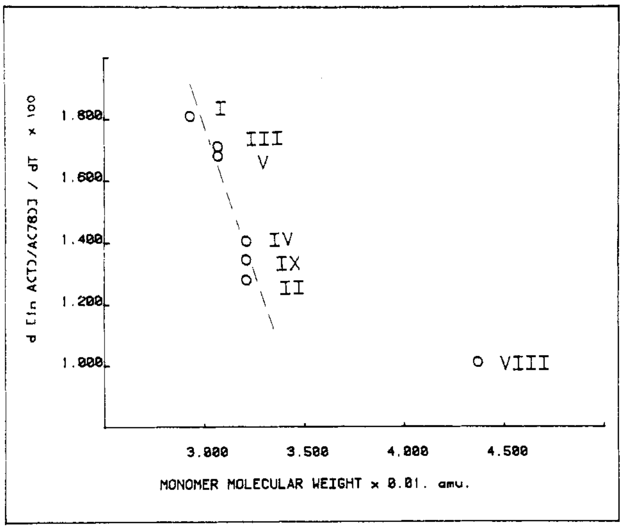
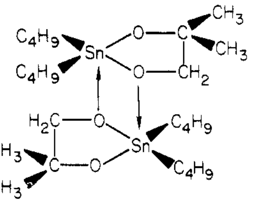


Figure 4. Correlation between the temperature dependence of the recoil-free fraction and the (monomer) molecular weight for related dibutyltin stannoxanes. The significance of the data point for VIII is discussed in the text.

tween the pure conformational isomers and the racemic mixtures. In this context it is interesting to note that the mean value of d[ln $f(T)$]/dT for IV and II in which the two methyl groups of the ring are bonded to two differect C atoms is just equal to the slope observed for IX in which the two methyl groups are bonded to the same carbon atom of the ring. In the latter compound, the expected steric requirements around the two ring carbon atoms are expected to favor an interaction of the type



since the steric hindrance for this interaction is presumed to be smaller than an interaction involving the other O atom. Since d[ln $f(T)$]/dT correlates reasonably well with the molecular weight of the monomer (i.e., II, IV, and IX) independent of either the presence of two conformational isomers or the distinction between the 3,4-dimethyl and 3,3-dimethyl structures, it is concluded that the *intermolecular* interactions in these solids are very weak or absent and that the formation of oligomers or infinite chain polymers in these diorganotin stannoxanes can be ruled out.

Perhaps the most persuasive data relating to the structural systematics of the subject compounds relates to those for samples VI and VIII. As will be noted from Figure 4, the temperature dependence of the recoil-free fraction for these compounds is lower than that observed for the other compounds listed, indicating a "stiffer" lattice or—more appropriately—a smaller mean square amplitude of vibration for the metal atom in these structures compared to the remaining members of the series. This observation can be readily understood on the basis of the assumption that in these cases, the fifth coordination site on Sn is occupied by the carbonyl oxygen of the ester rather than by the ether oxygen of the ring. This carbonyl oxygen is expected to be a better electron donor than the ring oxygen in the cyclic ligand. Such a structure would lead to a significantly greater molecular crowding around the metal atom and, hence, to a smaller vibrational amplitude at a given temperature. A testable consequence of this hypothesis is that there should be a red shift of the infrared-active $\nu_{C=O}$ for the ester involved in coordination to the metal atom. The appropriate portion of the infrared spectrum of VI is shown in Figure 5, from which it is noted that the C=O stretch, which is normally[19-21] observed as a sharp absorption at 1740–1750 cm^{-1}, is split into a doublet. The unshifted absorption at 1745 cm^{-1} is assigned to the ethyl ester carbonyl *not* coordinated to the metal, while the absorption red shifted to 1724 cm^{-1} is assigned to the ester carbonyl bonded to Sn. The near identity in the intensity of these two absorptions again confirms the postulated structure in which the solid consists of dimers in which the tin atom is five (but not six) coordinated.[22]

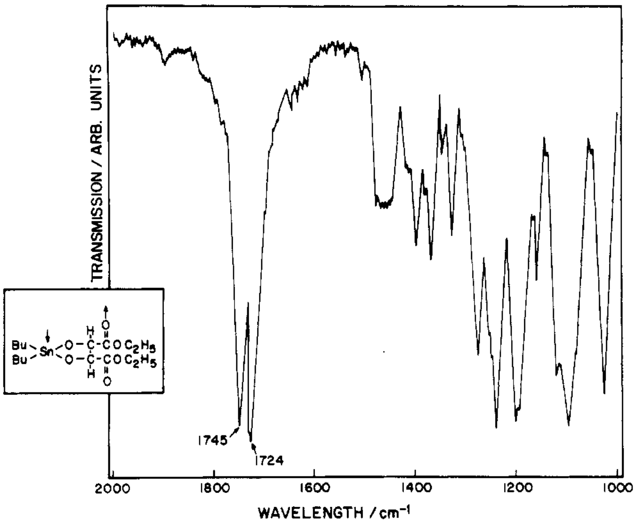


Figure 5. Portion of the infrared spectrum of VI in KBr. The two absorption maxima at 1745 and 1724 cm^{-1} are assigned to the C=O stretching frequency in the uncoordinated and the metal atom coordinated ethyl ester, respectively.

Finally, in terms of the pentacoordination around the metal atom in these bicyclic compounds, it is clear that the two Sn–C bonds cannot occupy a trans configuration (bond angle 180°) with respect to each other and hence that a temperature-dependent intensity asymmetry[23] of the two components of the Mössbauer quadrupole doublet is not expected. Detailed examination of the Mössbauer spectra has shown, in fact, that although there is an intensity asymmetry present in the spectra of the solids (presumably due to a crystal orientation effect), this asymmetry is temperature independent and does not reflect a dependence of the recoil-free fraction on the molecular symmetry axis in these dimeric species.

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[22] A reviewer has correctly pointed out that the systematics of: Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281, which relates the C–Sn–C bond angle in tetra-, penta-, and hexacoordinate diorganotin(IV) compounds to the observed quadrupole splitting parameters can be used to infer stereochemical information relevant to the present study. Applying these systematics to the dibutyl compounds under discussion leads to values of ∠C–Sn–C ranging from 118° for IX to 134° for VIII and are consistent with the inferences discussed above, if the assumption is made that in the (near) trigonal-bipyramidal pentacoordination around the metal atom, the equatorial plane contains two carbon atoms (of the butyl ligands) and one oxygen atom of the ring. The axial positions can then be envisioned as being occupied by the other oxygen atom of the ring and the donor oxygen atom of the second cyclic moiety.

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Synthesis and Spectra of (η^5-C_5H_5)$RhOs_2(CO)_9$ and H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$. Crystal Structure of (η^5-C_5H_5)$RhOs_2(CO)_9$

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From the reaction of $H_2Os_3(CO)_{10}$ with (η^5-C_5H_5)$Rh(CO)_2$, the trinuclear cluster (η^5-C_5H_5)$RhOs_2(CO)_9$ and the tetranuclear cluster H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ have been obtained in 45% and 42% yields, respectively. The crystal structure of (η^5-C_5H_5)$RhOs_2(CO)_9$ has been determined. Crystal parameters: space group $P\bar{1}$ (C_i^1, No. 2), $a = 9.128$ (2) Å, $b = 13.077$ (3) Å, $c = 8.224$ (2) Å, $\alpha = 106.94$ (2)°, $\beta = 113.51$ (2)°, $\gamma = 80.95$ (2)°, $V = 860.1$ (4) Å^3, $Z = 2$, mol wt = 800.5, $\rho_{calcd} = 3.090$ g cm^{-3}, $\mu_{calcd} = 157.37$ cm^{-1} for Mo Kα. The structural analysis is based upon 4497 independent reflections with $I > 3.0\sigma(I)$ collected on a CAD4 diffractometer at −80 °C over the range $4° \leq 2\theta \leq 60°$. Final $R_F = 0.057$ and $R_{wF} = 0.073$. In the crystalline state (η^5-C_5H_5)$RhOs_2(CO)_9$ has approximate C_s symmetry. The molecule consists of an Os_2Rh triangle with four terminal CO groups bound to each Os atom and a terminal CO and a η^5-C_5H_5 group bound to the Rh atom. Carbon-13 NMR spectra in solution are consistent with the solid-state structure. The tetranuclear cluster H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ was identified by means of FT-ICR mass spectrometry. It produces IR and NMR (^{1}H and ^{13}C) spectra that correspond very well to the solution spectra of the isoelectronic analogue H_2(η^5-C_5H_5)$CoOs_3(CO)_{10}$. These compounds are probably isostructural.

Introduction

Through the reaction of the electronically unsaturated cluster $H_2Os_3(CO)_{10}$ with metal carbonyls, we have prepared a number of new tetranuclear bimetallic clusters that contain an Os_3[1,2] unit. Among the compounds prepared in this way is H_2(η^5-C_5H_5)$CoOs_3(CO)_{10}$ which was obtained as the only identified product from reaction 1 in toluene.

$$H_2Os_3(CO)_{10} + (\eta^5\text{-}C_5H_5)Co(CO)_2 \xrightarrow{90\ °C} H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10} \quad (1)$$

In the present investigation we have examined the analogous reaction between (η^5-C_5H_5)$Rh(CO)_2$ with $H_2Os_3(CO)_{10}$. In this case not only was the tetranuclear cluster H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ obtained (42% yield)[2] but also the trinuclear compound (η^5-C_5H_5)$RhOs_2(CO)_9$ was also produced (45% yield). The preparation and spectra of these compounds and the crystal structure of (η^5-C_5H_5)$RhOs_2(CO)_9$ are described and discussed below.

Experimental Section

Preparation of H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ and (η^5-C_5H_5)$RhOs_2(CO)_9$. The starting materials $H_2Os_3(CO)_{10}$[3] and (η^5-C_5H_5)$Rh(CO)_2$[4] were prepared according to published methods. Toluene was distilled from CaH_2 before use.

Both $H_2Os_3(CO)_{10}$ (130 mg, 0.15 mmol) and (η^5-C_5H_5)$Rh(CO)_2$ (100 mg, 0.45 mmol) were placed in a 50-mL flask containing 20 mL of toluene. After the system was degassed, the mixture was stirred under vacuum at 90 °C for 3 days. A TLC spot check at this time indicated the complete consumption of $H_2Os_3(CO)_{10}$. Then toluene was removed under reduced pressure at room temperature on a rotary evaporator to leave a reddish brown residue. The residue was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on a thin-layer plate (2 mm silica gel). Elution with 1:4 benzene/hexane gave four bands. In order of decreasing R values, the bands were orange, brownish green, pink, and brown. The last two bands were not characterized due to the small quantities available.

The orange band was identified as (η^5-C_5H_5)$RhOs_2(CO)_9$ (55 mg, 45% yield based on $H_2Os_3(CO)_{10}$) from a single-crystal X-ray structure determination. Single crystals of (η^5-C_5H_5)$RhOs_2(CO)_9$ were obtained by crystallization from CH_2Cl_2/hexane at −15 °C: IR (η^5-C_5H_5)$RhOs_2(CO)_9$ in cyclohexane (ν_{CO}) 2095 (m), 2051 (s), 2020 (s), 1998 (m-w), 1968 (w) cm^{-1}.

The brownish green band was identified as H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ (60 mg, 42% yield based on $H_2Os_3(CO)_{10}$) from an analysis of its FT-ICR mass spectrum and comparison of its IR spectrum with that of H_2(η^5-C_5H_5)$CoOs_3(CO)_{10}$:[1] IR (H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ in cyclohexane (ν_{CO}) 2085 (m), 2063 (vs), 2042 (vs), 2010 (vs), 2000 (s(sh)), 1982 (m), 1972 (m), 1819 (m) cm^{-1}.

Infrared and NMR Spectra. Infrared spectra of solutions in matched cells were recorded on a Perkin-Elmer 457 spectrometer and were calibrated by using polystyrene as a standard. Proton and carbon-13 NMR spectra were obtained on a Bruker WH-300 spectrometer at 300.13 and 75.4 mHz, respectively. Chemical shifts are referred to $Si(CH_3)_4$ (^{1}H, τ 10.00; δ (^{13}C) 0.00).

Carbon-13 enriched samples of (η^5-C_5H_5)$RhOs_2(CO)_9$ and H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ for ^{13}C NMR spectra were prepared from enriched $H_2Os_3(CO)_{10}$ (ca. 25% ^{13}C) using the preparative procedures described above. A known amount of $Os_3(CO)_{12}$ was enriched by stirring it in refluxing toluene under a known amount

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