

Macrocycles Containing Tin. ^{119}Sn NMR Studies of Chloride Binding by Lewis Acidic Tin Compounds

Martin Newcomb,* Alex M. Madonik, Michael T. Blanda, and J. Kevin Judice

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received January 13, 1986

Three macrocyclic Lewis acidic hosts containing two symmetrically disposed dichlorostanna moieties (1-3; ring sizes, 18, 22, and 26 atoms, respectively) have been prepared as has an acyclic ditin model, 5,5,16,16-tetrachloro-5,16-distannaicosane (4). The complexation of 1-4 and dibutyltin dichloride (5) with chloride ion in acetonitrile was studied by ^{119}Sn NMR spectroscopy. Rapid exchange of chloride between tin atoms occurred at all ratios of chloride to host studied. An iterative computer program was used to provide estimates of the binding constants of 1, 2, 4, and 5 with chloride. Competition experiments were performed wherein two hosts competed for limited chloride ion, and the ^{119}Sn NMR spectra of the mixtures were analyzed to determine the relative amount of chloride bound by each host and hence the ratio of the binding constants for the two hosts. Good agreement between the relative binding constants found in the latter studies and the ratios of the absolute binding constants found in the former studies was found. The macrocyclic hosts exhibited small cooperative effects in binding chloride in comparison to 4 and 5 leading to an increase in binding energy. Host 1 binds chloride somewhat more strongly than hosts 2 or 3.

Over the past 15 years, macrocycle host-guest chemistry has evolved from a novelty to a well developed area of study. Extensive work has been reported in cation binding by basic macrocyclic hosts,¹ and reports of the binding of anions by charged macrocyclic hosts have appeared.^{1b} The binding of anions by neutral, multidentate Lewis acidic hosts is, with a few exceptions,² virtually unexplored. No reports of macrocyclic, Lewis acidic host binding of anion guests have appeared.

In this report we present studies of binding of an anion, chloride ion, by macrocycles which contain Lewis acidic tin atoms. ^{119}Sn NMR spectroscopy was used to study complexation of chloride by three macrocyclic hosts containing two Lewis acidic tin atoms, a ditin model, and a monotin model. An iterative computer program was used to provide estimates for the binding constants of chloride by the hosts, and competition experiments were performed to measure the relative binding constants of two hosts for chloride ion.

Preparation of Hosts

We have reported the syntheses of macrocycles containing two or four tin atoms.³ These macrocycles contained diphenylstanna moieties linked by polymethylene chains and, as such, were poor Lewis acids. However, conversion of the tin moieties of these compounds to dichlorostanna groups gave Lewis acidic species. Cleavage of the phenyl groups on tin was accomplished with high selectivity by treatment of the diphenylstanna compounds with excess anhydrous HCl in CH_2Cl_2 to give dichlorostanna macrocycles 1-3 (Scheme I). The compounds are sharp melting solids which show only one tin resonance in their ^{119}Sn NMR spectra.

(1) (a) Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 2. (b) Vögtle, F., Weber, E., Eds. *Host Guest Complex Chemistry/Macrocycles*; Springer-Verlag: Berlin, 1985.

(2) (a) Swami, K.; Hutchinson, J. P.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* 1984, 3, 1687-1694. (b) Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* 1983, 2, 909-914. (c) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* 1983, 2, 106-114. (d) Jurkschat, K.; Gielen, M. *Bull. Soc. Chim. Belg.* 1982, 91, 803-804. (e) Wuest, J. D.; Zacharie, B. *Organometallics* 1985, 4, 410-411. (f) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* 1985, 107, 6121-6123. (g) Katz, H. E. *J. Am. Chem. Soc.* 1985, 107, 1420-1421.

(3) Azuma, Y.; Newcomb, M. *Organometallics* 1984, 3, 9-14.

Scheme I

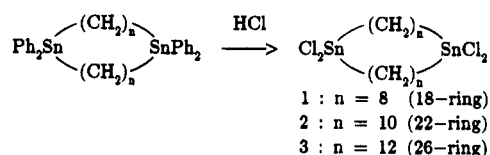
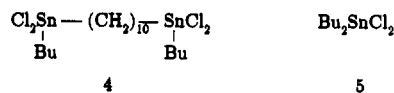


Table I. Observed ^{119}Sn NMR Chemical Shifts for Mixtures of Compounds 1-5 with Tetraethylammonium Chloride in Acetonitrile^a

compd	Cl ⁻ /Sn ratio					
	0	0.25	0.50	0.75	1.00	1.20
1	56.7	5.6	-39.3	-80.8	-120.0	-131.0
2	57.3	4.4	-39.1	-82.1	-119.0	-129.4
3	55.9		-37.1		-117.0	
4	47.5	0.4	-41.8	-82.5	-116.0	-125.0
5 ^b	34.7		-41.1		-102.2	-123.6 ^c

^a Measured at 29.8 MHz; concentrations of hosts 1-4 were 0.06-0.12 M. ^b Measured at 74.5 MHz; concentration of 5 was 0.16-0.20 M. ^c Cl⁻/Sn ratio was 1.5.

In preliminary studies, it appeared that 22-membered ring macrocycle 2 bound chloride more strongly than did 1 or 3. Thus, for comparison, acyclic model compound 4 was prepared. Dibutyltin dichloride (5) was used as a model for a monotin containing species.



^{119}Sn NMR Spectroscopy Studies of Chloride Binding by Acidic Hosts

Dialkyltin dichlorides bind chloride ion strongly, and it is possible to isolate a complex of 5 with tetraethylammonium chloride.⁴ However, in the polar aprotic solvent acetonitrile, this complex is soluble. Thus, we could study the effect on the ^{119}Sn NMR spectra of the Lewis acidic tin compounds 1-5 in acetonitrile as chloride was added. Compounds 1-5 in acetonitrile display chemical shifts in the range of 30-70 ppm relative to tetramethyltin which is a typical range for tetrahedral tin atoms con-

(4) Nicholson, J. W.; Douek, J. A.; Crowe, A. J. *J. Organomet. Chem.* 1981, 219, 309-316.

Table II. Concentration Effects on ^{119}Sn Chemical Shifts in Acetonitrile^a

sample ^b	^{119}Sn chem shift, δ					
	2.0 ^c	1.0 ^c	0.5 ^c	0.25 ^c	0.125 ^c	0.062 ^c
5	58.5	44.1	38.5	36.1	34.8	33.2
5 + 0.2Cl ⁻	12.2	1.7	1.4		0.9	0.9
5 + 0.8Cl ⁻	-90.8	-90.1			-84.9	-84.2
4		57.7	45.4	39.0	35.7	35.3
2		71.5	59.4	52.9	49.6	47.5

^a Measured at 74.5 MHz. ^b For samples containing chloride, the ratio of Cl⁻ to tin is given. ^c Sample concentrations in M.

taining two chlorides in this solvent.⁵ Upon addition of increments of tetraethylammonium chloride to the solutions, we observed only a single resonance which gradually shifted upfield as the ratio of chloride to tin was increased. The single signal indicated rapid exchange of chloride ion and that a weighted average signal of the various species present was observed. As the Cl⁻/Sn ratio was increased to greater than 1, the chemical shifts reached a plateau value at -124 to -131 ppm which is a typical range for pentacoordinate tin atoms.⁵

The ^{119}Sn NMR spectra of hosts 1-4 were measured as successive increments of 0.05 mol % of tetraethylammonium chloride were added. Data was collected for 17-27 individual ratios for each host. The chemical shift of the host was a smooth function of the Cl⁻/Sn ratio which was increased from 0.0 to 1.2. Table I lists representative chemical shifts at various ratios of Cl⁻/Sn. For dibutyltin dichloride (5) we also observed a smooth chemical shift change as incremental amounts of chloride were added up to 1.5 molar equiv (Table I).

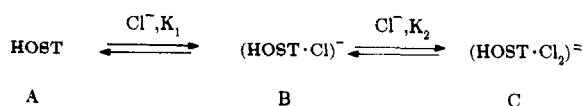
Concentration Effects and Inter- and Intramolecular Chloride Bridging

The effect of concentration on the ^{119}Sn chemical shift was studied in some detail with Bu₂SnCl₂ (5). The chemical shift of 5 in ca. 90% acetonitrile solution (remainder benzene-*d*₆ and Me₄Sn) was a function of the concentration of 5. The shift of the tin signal in a 2 M solution of 5 was at δ 58.5, but upon dilution the signal moved upfield ultimately to δ 33.2 for a 0.062 M solution (Table II). One can estimate that at infinite dilution of 5 the chemical shift would be ca. δ 32 in the solvent mixture used for this study. The concentration effect probably reflects changes in the amounts of intermolecular bridging between molecules of 5. Tin atoms ligated by chlorine on another molecule of 5 gave a downfield signal relative to those ligated only by solvent acetonitrile.

When concentration studies were performed on solutions of 5 containing 0.2 and 0.8 equiv of chloride ion per tin atom, similar but less dramatic chemical shift changes were observed (Table II). In the former case, dilution led to an upfield shift, but in the latter case, dilution led to a downfield shift. For the 0.2:1 (Cl⁻/Sn) solution, intermolecular bridging between molecules of 5 was the dominant effect. However, for the 0.8:1 (Cl⁻/Sn) solution, the amount of 5 complexed by chloride was more important.

Acetonitrile solutions of ditin compounds also displayed ^{119}Sn NMR chemical shifts which were sensitive to concentration and similar in magnitude to that observed for 5. Examples for ditin acycle 4 and macrocycle 2 are given in Table II. Again there was an upfield shift observed upon dilution of these species which apparently reflects reduc-

Scheme II



tion in the amount of intermolecular chloride-bridged species. While the chemical shift for 4 at infinite dilution would be estimated at about δ 34, the chemical shift of the macrocycle at infinite dilution would be about δ 46. It is noteworthy that the δ values for ditin 4 were almost identical with those for monotin 5 at twice the concentration. Apparently this represents little intramolecular bridging in 4 but some intramolecular bridging in 2; as a crude approximation, the effective concentration of one tin atom in 2 relative to the other tin atom is about 1 M if the spectral change at infinite dilution arose only from intramolecular effects.

One final point should be made concerning solvent effects on ^{119}Sn NMR chemical shifts. In studies run at 29.8 MHz, we used solvent mixtures which were about 75% acetonitrile (remainder benzene-*d*₆ and Me₄Sn). For the 74.5-MHz measurements, the solvent mixture was about 90% acetonitrile. The effect of increasing the concentration of the Lewis basic solvent acetonitrile from 75% to 90% can be seen in the measurements given in Tables I and II. The ^{119}Sn NMR chemical shifts observed with 0.12 M solutions of 2 and 4 in 75% acetonitrile with no added chloride were 8-11 ppm downfield from those of the corresponding concentration in 90% acetonitrile. Because of the relatively large concentration effects on chemical shifts at high concentrations of hosts, most of our studies were run at about 0.1 M where the concentration effect was minimized but where spectra could still be obtained with relative ease.

Qualitative Evaluation of Chloride Binding

The measured chemical shifts in Table I are weighted averages of all of the tin species in solution. We made the simplifying assumption that for the host compounds 1-4 the predominant species in solution were uncomplexed species (A), the monochloride complex (B), and the dichloride complex (C) (Scheme II). The ^{119}Sn NMR chemical shift of A was measured in the absence of added chloride salt, and the ^{119}Sn NMR chemical shift of C could be estimated as the chemical shift observed in the presence of excess chloride salt. With these assumptions one can make two qualitative observations concerning chloride complexation.

(1) The binding constants of the ditin hosts for chloride are large. In Table I for hosts 1-4, the $\Delta\delta$ observed between 0.0 and 0.5 equiv of Cl⁻ per host was greater than one-half of the $\Delta\delta$ observed when excess chloride was present and the limiting values of δ were observed when only ca. 1.2 equiv of chloride were added. Therefore, both the first and second binding constants must be large. The binding constants of 1-4 are greater than that of monotin model 5 because ca. 1.5 equiv of chloride were required to obtain the limiting δ value for 5.

(2) Cooperative effects apparently were present in 1:1 complexes of chloride and hosts. For hosts 1-4, the chemical shifts at Cl⁻ to tin atom ratios of 0.5 were somewhat greater than one-half of the total chemical shift difference seen between chloride to tin atom ratios of 0 and 1. Within the constraints of the assumption that A, B, and C are the predominant species in solution and given the smooth chemical shift changes observed from zero to excess chloride, it is required that the 1:1 complex (B) reached its maximum concentration in the vicinity of a 1:1 molar

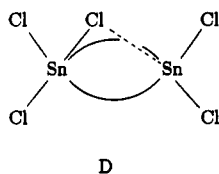
(5) Smith, P. J.; Tupciauskas, A. P. *Annu. Rep. NMR Spectrosc.* 1978, 8, 291-370. Petrosyan, V. S. *Prog. Nucl. Magn. Reson. Spectrosc.* 1977, 11, 115-148. Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* 1985, 16, 73-186.

Table III. Optimized Solutions for the Chemical Shifts for δ_A , δ_B , and δ_C and Binding Constants K_1 and K_2 Found by Generalized Curve Fitting^a

host	δ_A	δ_B	δ_C	K_1, M^{-1}	K_2, M^{-1}
1	56.4	-48.0	-127.2	814	863
2	55.7	-48.2	-129.3	684	556
4	46.0	-48.2	-130.8	427	527
5 ^b	34.7		-124.5	204	

^a Model in Scheme II; initial values: δ_A = observed value in Table I for Cl/Sn = 0, δ_B -48, δ_C -132; $K_1 = K_2 = 500 M^{-1}$. ^b Model in Scheme III; initial values: δ_A 34.7, δ_C -124; $K = 500 M^{-1}$.

ratio of chloride to host. Either (a) the binding constant K_1 in Scheme II is much larger than K_2 and at chloride to tin atom ratios of 0.5 essentially only B was present, or (b) in the complex B the bound chloride ion interacted with the remote tin atom (structure D), or (c) there was a combination of these two effects. Since intermolecular bridging apparently existed in macrocyclic ditin compounds containing no added chloride, structure D is reasonable.



By our assumption that A, B, and C are the predominant species in solution, we have excluded the possibility that intermolecular bridging of two tin compounds by chloride leads to the observed chemical shift values at 0.5 ratios of chloride to tin atoms. On the basis of the dilution results discussed above, this assumption is sound at the low concentrations studied.

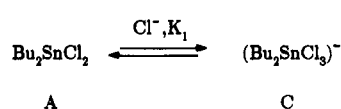
Quantitative Evaluation of Chloride Binding

In principle, it should be possible to extract from the NMR data the binding constants K_1 and K_2 in Scheme II. With the assumption that species A, B, and C are the predominant species in solution, we wrote an iterative computer program based on a published model for generalized curve fitting⁶ which was used to calculate the association constants (see Appendix). The program used the actual concentrations of reagents and the measured chemical shifts, and it was flexible enough to permit several models for binding. In its most general form it could solve for the five variables δ_A , δ_B , δ_C , K_1 , and K_2 to find the best fit for the NMR data where the observed chemical shift is a weighted average of the shifts for A, B, and C. Any or all of the variables could be either fixed or varied by predetermined initial amounts in the fitting procedure.

Since we could estimate the chemical shift of A (δ_A) and that of C (δ_C) with reasonable certainty, we hoped that the program would converge on consistent values of δ_B and K_1 and K_2 . However, the program failed to converge to a unique minimum solution when δ_B , K_1 , and K_2 were varied. Essentially, there were two or more minima found for the complexations of 1, 2, and 4 with chloride, and these minima were a function of the initial value assigned to δ_B .

However, it was possible to solve the data for hosts 1, 2, and 4 in an acceptable manner. When we assigned an initial value of δ_B -48 and then performed successive iterations altering first the three chemical shift values and then the two association constants, we consistently found solutions for the five variables which gave the smallest

Scheme III



errors relative to the observed data (χ^2 test). With the caveat that these values are constrained to the region surrounding δ_B -48, the results are given in Table III. It was satisfying that when permitted to vary, the values for the chemical shifts of species A and C were found to be quite close to the experimental values. The data for host 3 was not successfully treated by our program which consistently minimized the solution to give an unreasonable chemical shift for B.

The binding constant for the acyclic, monotin model 5 was determined by the iterative program where we assumed that only the species in Scheme III were present. The program converged on the reasonable value listed in Table III.

There is a potential problem with our approach for determining the binding constants. Since a large concentration effect on ^{119}Sn δ values was observed and since, in the case of 5, the concentration effect diminished and eventually reversed as the ratio of chloride to tin was increased, it is possible that our approach contains an undetermined systematic error. In principle, however, such an error need not be present. We tested for such an error by conducting one study with 5 at substantially higher concentrations where intermolecular bridging had been demonstrated. When data collected on 0.5 M solutions of 5 was used to calculate K and δ_A was fixed at the experimentally observed value, we obtained an unreasonably low value for δ_C (-138) and a corresponding low value for K ($60 M^{-1}$) for the best fit. However, when the same data was treated with no restrictions on δ_A , the optimized value for δ_A was 3 ppm upfield from the experimental value, but the value of δ_C remained at -124 ppm and the value of K was $190 M^{-1}$, in good agreement with values listed in Table III. Apparently, in this case, the program successfully treated data which was obviously skewed at low chloride to tin ratios because of intermolecular bridging.

From the calculated values for the association constants, it appears to be sound to conclude that the ditin hosts 1, 2, and 4 complex chloride with decreasing strength and that the ditin hosts bind chloride more strongly than 5. Further, the results in Table III suggest that the 18-membered and 22-membered ring macrocycles (1 and 2) exhibit a slight "macrocyclic effect" in that they bind chloride more strongly than the acyclic ditin host 4. These data are also consistent with a small "size-selective effect" in that the 18-membered ring host binds chloride somewhat more effectively than the 22-membered ring host.

The results in Table III still must be viewed with caution. Since K_1 and K_2 were both large and similar in value, plots of chemical shift vs. chloride concentration were only slightly curved. This is exactly the type of data which the multiparameter program might fit poorly. Despite our reservations concerning the *absolute* values for K 's, the results of our competitive binding studies support the conclusions obtained from the results in Table III and show that the *relative* values for K_1 's in Table III are accurate.

Direct Determination of Relative Binding Efficiencies

One conclusion which is inescapable from either the qualitative or quantitative estimates of binding is that the binding constants are large. For comparisons between two hosts, direct competition experiments wherein two hosts

(6) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

Table IV. Results of Competitive Binding Experiments^a

host X	host Y	Cl, ^b mol %	δ_X	δ_Y	K_{1X}/K_{1Y} ^c	K_{1X}/K_{1Y} ^d (calcd) ^d
1	4	0.05	40.5	38.7	1.81	1.91
		0.15	17.6	22.8	1.52	
		0.40	-31.2	-20.3	1.39	
		0.80	-97.1	-90.1	1.42	
2	4	0.30	1.2	4.9	1.34	1.61
		0.40	-20.7	-14.5	1.24	
		0.60	-61.4	-53.1	1.36	
3	4	0.20	17.2	18.0	1.41	
		0.40	-20.4	-15.2	1.41	
		0.80	-90.3	-82.9	1.25	
1	2	0.30	-2.1	4.0	1.23	1.18 (1.1) ^e
1	5 ^f	0.60	-63.2	-62.8	1.14	4.0
		0.4	-14.7	-6.4	2.45	
4	5 ^f	0.10	35.7	35.2	1.71	2.1

^a See text for description of the experiment and rationale. ^b Mol % of chloride relative to the sum of the moles of hosts. ^c Calculated from eq 3. ^d Calculated from the association constants in Table III. ^e Calculated from the ratios of experimental relative association constants of 1 to 4 (estimated at 0.3 mol % Cl⁻) and 2 to 4 (at 0.30 mol % Cl⁻). ^f Concentration of 5 was 0.5 M.

compete for limited chloride were desired. Since chloride exchange between tin sites was rapid leading to only one ¹¹⁹Sn NMR signal for the host, such experiments seemed feasible. In fact, these studies proved not to be difficult. When two hosts were mixed in a 2:1 ratio in acetonitrile and a small amount of tetraethylammonium chloride was added, we observed two signals in the ¹¹⁹Sn NMR spectrum. The peaks' intensities were in a 2:1 ratio, and signals were readily assigned. The measured chemical shifts for each host were compared to plots of chemical shift vs. Cl⁻/Sn ratio obtained previously. This permitted us to assign the number of moles of chloride bound by each host and to calculate the complexed and free mole fractions of each host.

At low chloride to host ratios, we may assume that little of the dichloride complex C in Scheme II was present and that the amounts of chloride bound by each host reflected the K_1 of the host. The K_1 's for hosts X and Y can be compared from the chemical shift data as shown in the simple derivation below. It is noteworthy that, to a first approximation, the absolute amounts of a host used should not be important since only the ratio of complexed to free host are needed in eq 3. In practice this was shown to be true by changing the ratio of host X to host Y from 2:1 to 1:2; no noticeable effect was seen in the calculated ratio of binding constants. It also should be noted that our approach is an oversimplification which can apply only at low chloride to host ratios. As the chloride to host ratio is raised, the second complexation constants will become important and the percentage of chloride bound by host X and host Y should change.

$$K_{1X} = [X \cdot Cl^-]/[X][Cl^-] \quad K_{1Y} = [Y \cdot Cl^-]/[Y][Cl^-] \quad (1)$$

$$[Cl^-] = [X \cdot Cl^-]/[X]K_{1X} = [Y \cdot Cl^-]/[Y]K_{1Y} \quad (2)$$

$$K_{1X}/K_{1Y} = ([X \cdot Cl^-]/[X])([Y]/[Y \cdot Cl^-]) \quad (3)$$

Table IV lists the results of the competitive binding studies with ditin hosts 1-4. The chloride to host ratio was maintained below 1:1, but one can see that as this ratio increased the apparent relative binding constants of the two hosts were altered as was expected. We also have listed the calculated value of K_{1X}/K_{1Y} using the constants from Table III.

Even qualitative observations of the ¹¹⁹Sn NMR spectra of the competition experiments with the cyclic hosts 1-3

Table V. Host-Chloride Binding Energies in Acetonitrile^a

Binding Energies			
host	$-\Delta G$, kcal/mol	host	$-\Delta G$, kcal/mol
1	4.02	4	3.63
2	3.92	5	3.20
Relative Binding Energies			
$-\Delta\Delta G$, kcal/mol			
hosts	from Table III	from Table IV	
1 vs. 4	0.38	0.19-0.35	
2 vs. 4	0.28	0.13-0.18	
3 vs. 4		0.13-0.20	
1 vs. 2	0.10	0.08-0.12	
1 vs. 5	0.83	0.54-0.60	
4 vs. 5	0.44	0.32	

^a At 25 °C, calculated for the first binding constants for the ditin hosts.

vs. acyclic host 4 clearly showed that the cycles bound chloride more strongly than 4. The signal from 4 in the absence of chloride was upfield of the signals from 1-3 in the absence of chloride, yet at chloride mol % values of 0.15 or greater, the signal from the cyclic host had moved upfield of that from 4. The results in Table IV show the same trends we had seen in the values of the association constants listed in Table III for hosts 1, 2, and 4. Macrocyclic effects and a small size selective effect are seen in binding chloride. The favorable comparisons of K_{1X}/K_{1Y} determined for the ditin compounds in the competition experiments against those calculated from the values in Table III are important because they indicate that the assumptions and restrictions imposed in the calculations in Table III for the ditin compounds were reasonable, and they suggest that the relative values of K_1 for 1, 2, and 4 found by our method are reasonably accurate.

Competitive binding experiments with dibutyltin dichloride (5) and a ditin compound were also possible. Table IV includes the results when hosts 1 and 4 competed with 5 for limited chloride. In these experiments, the concentration of 5 was about five times that of 1 or 4, and we used data from our high concentration study of 5 to estimate the percentage of complexed 5. Since intermolecular bridging between two molecules of 5 and between 5 and a ditin host will occur at this concentration, the results should be less accurate than those found in the other competition studies. The ratios of K_X/K_Y were lower than predicted from the data in Table III, however, if bridging between 5 and a ditin host gave the expected downfield shift for the ditin, then we underestimated the amount of chloride complexed by the ditin host in our calculations. The results of the two competition experiments with 5 against 1 and 4 are consistent with the competition experiment between 1 and 4. That is, the quotient of the relative binding constants for 1 and 5 (at Cl⁻/Sn = 0.2) divided by that for 4 and 5 (at Cl⁻/Sn = 0.1) is 1.57, a good agreement with the relative binding ratio of 1 to 4 (at Cl⁻/Sn = 0.15) of 1.52. This kind of consistency reinforces our conclusion that the competition experiments gave reasonably accurate ratios of binding constants for the ditin compounds.

The free energies ($-\Delta G$) of the first binding constants for complexing chloride in acetonitrile for 1, 2, 4, and 5 may be calculated from the data in Table III, and the differences in free energies of the binding constants ($-\Delta\Delta G$) may be calculated from the data in Tables III and IV. Table V contains the results. Whereas doubling the number of tin atoms in acycle 4 relative to 5 essentially only doubles the binding effect, small cooperative effects in the binding constants for chloride by the macrocyclic compounds are

present. These increases in binding energies for the macrocycles relative to 4 and 5 exist despite the fact that intramolecular bridging apparently is present in the free macrocycles but not in 4 or 5.

Conclusion

The Lewis acidic ditin hosts 1-4 display the same trends in binding chloride ion in acetonitrile that basic hosts display in binding cations although the effects are greatly attenuated. A macrocyclic effect appears to exist in 1-3 relative to 4, and there is some evidence that a small size-selective effect exists in 1 relative to 2 and 3. Given that the hosts studied in this work are quite flexible providing little organization for binding, that they contain only two binding sites, and that the binding sites are spaced apart by 8-12 methylene groups, these results are encouraging. It should be expected that both increasing the rigidity of the host and the number of binding sites will provide more dramatic effects.

Experimental Section

General Data. Reagents were purchased from Aldrich Chemical Co. and Thiokol Corp. Dibutyltin dichloride (5) was used without further purification. NMR spectra were recorded at 22-25 °C on a Varian FT-80 (¹³C and ¹¹⁹Sn) and a Varian XL-200 (¹¹⁹Sn) with full proton decoupling. To avoid negative nOe in the ¹¹⁹Sn NMR spectra, the decoupler was gated off during a 1.5-s delay between pulses. Chemical shifts are reported in parts per million relative to internal (CH₃)₄Si for ¹³C NMR spectra and relative to internal (CH₃)₄Sn for ¹¹⁹Sn NMR spectra. Analyses were performed by Galbraith Laboratories, Inc.

Synthesis of 5,5,16,16-Tetraphenyl-5,16-distannaicosane. To a stirred solution of 1,12-dibromo-1,1,12,12-tetraphenyl-1,12-distannadodecane³ (2.25 mmol, 1.89 g) in 25 mL of THF (distilled from potassium-benzophenone under nitrogen) at 0 °C under nitrogen was added over 1.25 h a solution of butylmagnesium bromide (42 mL of a 0.112 M solution in THF, 4.7 mmol). The stirred solution was allowed to reach room temperature overnight. The reaction mixture was cooled to 0 °C and treated with 50 mL of saturated aqueous ammonium chloride solution. The aqueous layer was extracted twice with ether (50 mL), and the combined organic phases were washed with brine (50 mL) and dried over MgSO₄. Solvents were distilled in vacuo, and the resulting residue was purified by reverse phase chromatography³ eluting with ca. 3.5:1 methanol/THF to give 1.40 g (1.75 mmol, 78%) of the desired product. ¹³C NMR (CDCl₃): δ 140.3, 136.6, 128.2, 128.1, 34.2, 29.4, 29.0, 27.2, 28.8, 26.6, 13.5, 10.4, 10.2. ¹¹⁹Sn NMR (CDCl₃): δ -72.0. Anal. Calcd for C₄₂H₅₈Sn₂: C, 63.03; H, 7.31. Found: C, 62.88; H, 7.33.

Synthesis of 5,5,16,16-Tetrachloro-5,16-distannaicosane (4). To a solution of 5,5,16,16-tetraphenyl-5,16-distannaicosane (1.73 mmol, 1.38 g) in 50 mL of dry dichloromethane at -78 °C with stirring was added dropwise 35 mL of a standardized HCl solution in dichloromethane (0.22 M, 7.7 mmol) over 0.3 h. The stirred solution was allowed to reach room temperature overnight. Evaporation of the solvent followed by recrystallization from ether gave a white crystalline product in 60% yield (0.65 g, 1.03 mmol); mp 87-88 °C. ¹³C NMR (CDCl₃): δ 32.8, 28.9, 28.6, 26.9, 26.6, 26.0, 24.5, 13.2. ¹¹⁹Sn NMR (CDCl₃): δ 123.5. Anal. Calcd for C₁₈H₃₈Cl₄Sn₂: C, 34.12; H, 6.04; Cl, 22.38. Found: C, 34.17; H, 6.03; Cl, 21.93.

Preparation of Hosts 1-3. We have reported the preparation of the 1,1,*n,n*-tetraphenyl-1,*n*-distannacycloalkanes.³ Gaseous HCl was bubbled through methylene chloride at -78 °C to give a saturated solution. The solution was allowed to warm to room temperature, and an aliquot was removed, added to water, and titrated with a standardized base solution to determine the concentration of acid. The CH₂Cl₂ solution of HCl was added to a solution of the tetraphenyldistanna macrocycle in CH₂Cl₂ at -78 °C such that ca. 5 molar equiv of acid were added in all. After 6-8 h, the reaction mixture was allowed to warm to room temperature. The reaction mixture was concentrated under reduced pressure to give a crude solid product. Recrystallization from CH₂Cl₂-hexane (ca. 1:3, v/v) gave white, crystalline products

which were characterized by ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy. ¹H NMR spectra were not informative. There was no indication of bond cleavage between the tin atoms and the methylene units in the macrocycles in the ¹³C and ¹¹⁹Sn NMR spectra.

Characterization of 1,1,10,10-tetrachloro-1,10-distannacyclooctadecane (1): mp 84-85 °C. ¹³C NMR (CDCl₃): δ 32.8, 28.4, 27.8, 24.7. ¹¹⁹Sn NMR (CDCl₃): δ 121.9. Anal. Calcd for C₁₆H₃₂Cl₄Sn₂: C, 31.84; H, 5.34; Cl, 23.49. Found: C, 32.15; H, 5.28; Cl, 22.53.

Characterization of 1,1,12,12-tetrachloro-1,12-distannacyclocosane (2): mp 95-97 °C. ¹³C NMR (CDCl₃): δ 33.1, 29.0, 28.7, 28.0, 24.8. ¹¹⁹Sn NMR (CDCl₃): δ 123.1. Anal. Calcd for C₂₀H₄₀Cl₄Sn₂: C, 36.41; H, 6.55; Cl, 21.50. Found: C, 36.67; H, 6.39; Cl, 20.90.

Characterization of 1,1,14,14-tetrachloro-1,14-distannacyclohexacosane (3): mp 97-99 °C. ¹³C NMR (CDCl₃): δ 33.1, 29.0, 28.9, 28.7, 28.0, 24.8. ¹¹⁹Sn NMR (CDCl₃): δ 123.4. Anal. Calcd for C₂₄H₄₈Cl₄Sn₂: C, 40.27; H, 6.76; Cl, 19.81. Found: C, 40.42; H, 6.64; Cl, 19.94, 19.61.

Equilibrium Binding Constants. ¹¹⁹Sn NMR spectra were recorded at 29.8 MHz in 75% acetonitrile solutions or at 74.5 MHz in 90% acetonitrile solutions. Host 1-5 (0.25 mmol) was dissolved in dry acetonitrile, and the solution was filtered through a plug of Celite into a 2-mL volumetric flask. Benzene-*d*₆ and (CH₃)₄Sn were added, and additional acetonitrile was added to the mark. After measurement of the initial chemical shift, successive aliquots of tetraethylammonium chloride solution were added via syringe, and the NMR spectrum of each resulting solution was recorded. In some cases a second sample of the host (0.25 mmol) was prepared, diluting to 2 mL by using 1.00 mL of the stock chloride solution giving a 1:1 molar ratio of host and chloride as a starting point for further chloride additions; small discrepancies (1-4 ppm) were noted between the chemical shift measured for this solution and that measured for the previous sample after 10 additions of 0.10-mL aliquots of the stock chloride solution.

¹¹⁹Sn NMR Competition Studies. Spectra were recorded at 74.5 MHz. The competition experiments were performed by mixing two hosts (ca. 0.3 mmol of one host and ca. 0.6 mmol of the second) in 5 mL of acetonitrile with benzene-*d*₆ and (CH₃)₄Sn. A weighed amount of tetraethylammonium chloride was added, and the spectrum was recorded.

Acknowledgment. We are grateful to the Office of Naval Research for financial support of this work. We thank an anonymous reviewer for useful suggestions.

Appendix. Determination of Equilibrium Binding Constants

The ¹¹⁹Sn NMR chemical shift data was fit by using an iterative procedure based on the gradient search program given by Bevington.⁶ This procedure attempts to minimize χ², which measures the departure of the calculated chemical shift values from the observed values. Since all tin species were in rapid equilibrium, the chemical shift was calculated as the weighted average of the chemical shifts of the individual species assumed to be present.

For the single equilibrium in Scheme III, the necessary concentrations could be deduced from the observed chemical shift as follows:

$$[A] = ((\delta_{\text{obsd}} - \delta_C) / (\delta_A - \delta_C)) [Sn]_{\text{total}}$$

$$[C] = ((\delta_{\text{obsd}} - \delta_A) / (\delta_C - \delta_A)) [Sn]_{\text{total}}$$

The concentrations so calculated could be used to estimate the value of *K*, the equilibrium constant. Once an estimate of *K* was available, the concentrations of A and C for all the Cl/Sn ratios studied could be calculated from the appropriate equilibrium expression:

$$[C] = (-b - (b^2 - 4c)^{1/2}) / 2$$

$$[A] = [Sn]_{\text{total}} - [C]$$

$$-b = [Sn]_{\text{total}} + [Cl^-]_{\text{total}} + 1/K$$

$$c = [\text{Sn}]_{\text{total}}[\text{Cl}^-]_{\text{total}}$$

The chemical shift was then calculated for each point

$$\delta_{\text{calcd}} = ([\text{A}]\delta_{\text{A}} + [\text{C}]\delta_{\text{C}})/([\text{A}] + [\text{C}])$$

and the results were compared to the experimental values. The fit parameters, K , δ_{A} , and δ_{C} , were varied iteratively using the gradient search procedure to find the best fit. Since δ_{A} and δ_{C} were known from the limiting values of the observed chemical shift, the best value of K could be found rapidly.

For two coupled equilibria (Scheme II), the situation was more complex. The chemical shift is given by

$$\delta_{\text{calcd}} = ([\text{A}]\delta_{\text{A}} + [\text{B}]\delta_{\text{B}} + [\text{C}]\delta_{\text{C}})/([\text{A}] + [\text{B}] + [\text{C}])$$

Using the equilibrium expressions and the substitutions

$$[\text{A}] = [\text{Sn}]_{\text{total}} - [\text{B}] - [\text{C}]$$

$$[\text{Cl}^-] = [\text{Cl}^-]_{\text{total}} - [\text{B}] - 2[\text{C}]$$

one obtains the following equations for $[\text{B}]$ and $[\text{C}]$:

$$[\text{B}] = (-b - (b^2 - 4c)^{1/2})/2$$

$$-b = [\text{Sn}]_{\text{total}} + [\text{Cl}^-]_{\text{total}} - 3[\text{C}] + 1/K_1$$

$$c = -[\text{C}](2[\text{Sn}]_{\text{total}} + [\text{Cl}^-]_{\text{total}} - 2[\text{C}]) + [\text{Sn}]_{\text{total}}[\text{Cl}^-]_{\text{total}}$$

$$[\text{C}] = [\text{B}]([\text{Cl}^-]_{\text{total}} - [\text{B}]) / (2[\text{B}] + 1/K_2)$$

Rather than solving this pair of simultaneous equations explicitly for $[\text{B}]$ and $[\text{C}]$, we evaluated them iteratively by the "fixed-point" method.⁷ An initial estimate for $[\text{C}]$ was used in calculating $[\text{B}]$, this new value of $[\text{B}]$ was used to recalculate $[\text{C}]$, and so on until convergence gave an unchanging value for the calculated chemical shift. In this way, δ_{calcd} was obtained for the full range of chloride/tin ratios for which the chemical shift had been measured experimentally.

In practice, the fixed-point iteration did not converge reliably for large K 's (on the order of 100 or more) when

the ratio of added halide ion to tin sites was greater than 1:1 (i.e., a 2:1 molar ratio of added Cl^- to ditin compound), so the few data points at higher ratios had to be neglected in the computer fit. This may reflect a shortcoming of the method. We believe that when species C becomes the predominant species, a lack of convergence can result from a sign change in the derivative of the expression for $[\text{C}]$.

The best values for K_1 and K_2 were determined by comparison of the observed and calculated chemical shift values, using the gradient search procedure. The results proved to be quite sensitive to the initial choice of δ_{B} , the chemical shift value assigned to the 1:1 complex of ditin host and chloride. Allowing the program to vary this parameter did not provide a unique best value. Comparison of the results for the compounds 1, 2, and 4 suggested that -48 ppm was a good estimate for the chemical shift of species B, and this value was used to obtain optimized equilibrium constants for the purposes of comparison among the ligands. Additional improvement in the fit to the experimental data could be achieved by allowing the computer program to vary the other two chemical shift parameters, δ_{A} and δ_{C} , after the equilibrium constants had been calculated. Only small changes in these two parameters were necessary to obtain the best possible fit, a reassuring result since their values were expected to lie close to the observed chemical shifts for the free ligands (δ_{A}) and the ligands in the presence of excess added chloride (δ_{C}).

The χ^2 statistic provides an estimate of reliability of our mathematical model. Assuming a standard deviation of ± 2 ppm in the chemical shift measurements resulting mainly from errors in the measured concentrations, we obtained reduced χ^2 values (χ^2 divided by the number of degrees of freedom, in our case usually 15-21 data points and five parameters) below 0.5. This permits good confidence (greater than 90% probability) in the validity of our mathematical model.

Registry No. 1, 105162-88-7; 2, 105182-65-8; 3, 105162-89-8; 4, 105162-90-1; 5, 683-18-1; tetraethylammonium chloride, 16887-00-6; 5,5,16,16-tetraphenyl-5,16-distannaicosane, 105162-91-2; 1,12-dibromo-1,1,12,12-tetraphenyl-1,12-distannadodecane, 87518-49-8; 1,1,10,10-tetraphenyl-1,10-distannacyclooctadecane, 87531-98-4; 1,1,12,12-tetraphenyl-1,12-distannacyclodocosane, 87518-37-4; 1,1,14,14-tetraphenyl-1,14-distannacyclohexacosane, 87518-38-5.

(7) See, for example: Conte, S. D.; de Boor, C. *Elementary Numerical Analysis; an Algorithmic Approach*, 2nd ed., McGraw-Hill: New York, 1972, p 84.

Diels-Alder Reactions Utilizing (Ferra- β -diketonato)BF₂ Complexes Containing Alkynyl Substituents as Activated Dienophiles

Charles M. Lukehart* and LouAnn Sacksteder

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Received June 11, 1986

Two (ferra- β -diketonato)BF₂ complexes containing propynyl substituents on the ferra-chelate ring have been prepared. The propynyl substituents react with cyclopentadiene at room temperature to give the corresponding norbornadienyl Diels-Alder cycloaddition products. A complex containing both propynyl and methacryl substituents on the ferra-chelate ring exhibits chemoselectivity and stereoselectivity in Diels-Alder adduct formation.

Introduction

We have reported recently that (ferra- β -diketonato)BF₂ complexes which have alkenyl substituents attached to the ferra-chelate ring react as activated dienophiles in Diels-Alder cycloaddition reactions.¹ For example, the addition

of dimethylbutadiene to such a complex containing a methacryl substituent occurs at a rate 50 times greater

(1) Lenhart, P. G.; Lukehart, C. M.; Sacksteder, L. A. *J. Am. Chem. Soc.* 1986, 108, 793-800.