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Multidentate Lewis Acids: Theoretical Study of Anion Binding by Organoboron Macrocyclic Hosts

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Abstract: Molecular orbital (AM1) calculations have been carried out on two classes of multidentate boron-containing macrocycles and their inclusion complexes with H^-, F^-, Cl^-, and O^{2-}. One class of macrobicycle (I) is represented by $B[(CH_2)_n]_3B$, where $n = 3$–10. On the basis of calculated standard enthalpies of reaction, hydride is bound to approximately the same extent by the hosts with $n = 4$–6, fluoride by hosts with $n = 5$, 6, and chloride by hosts with $n = 6$, 8, and oxide is bound by hosts with $n \geq 4$. While some size selectivity is apparent, the decrease in binding energy as n increases is generally not pronounced, and none of the anions show a marked preference for any particular host in this series. Greater anion specificity was observed in a second class (II) of macrotricyclic hosts, which contain four boron Lewis acid sites: $B_4[(CH_2)_n]_6$, where $n = 2$–4. In this series, hydride and oxide favor $n = 2$, while fluoride and chloride favor $n = 3$. Substantial increases in binding energy, compared to the case for class (I) complexes, are observed for class (II) complexes in which the anion is bound to more than two boron atoms. This occurs for chloride with $n = 3$ and oxide with $n = 2$ or 3. All boron atoms in the neutral hosts are sp^2 hybridized. Successful anion inclusion in both class (I) and class (II) macrocycles occurs with a decrease in B–B distance and partial rehybridization ($sp^2 \rightarrow sp^3$) of one or more boron atoms.

Introduction

The vast majority of macrocycles contain nitrogen and/or oxygen donor atoms.[2] The coordination chemistry of these macrocycles principally involves interactions with cations[2a] and, in some cases, neutral molecules.[2c] Anion coordination by such ligands almost always involves prior protonation of nitrogen atoms.[2a,3] Direct anion coordination by neutral hosts is much less common, but interest in the area of multidentate Lewis acids is rapidly increasing.[4–7] Recent studies have employed mercury,[4] tin,[5] and boron[6] as Lewis acid centers. Although almost all of the multidentate Lewis acids synthesized up until now have been bidentate, there are a few examples with three,[4a] four,[4b,5c] or even six[4d] Lewis acid sites. The bidentate boron hosts[6] involve trigonal boron sites which have been shown to add bridging guests such as hydride,[6b–d] fluoride,[6c,d] chloride,[6e] and pyrimidine.[6f]

Extensive studies of tin-containing macrobicycles[5] ($ClSn[(CH_2)_n]_3SnCl$, $n = 6$–12) include determinations of equilibrium constants for the inclusion of fluoride,[5b] chloride,[5a,c,e] and bromide[5a] in several ligands in the above series. Here, some degree of anion specificity has been observed. For example, the $n = 6$ member of the series binds fluoride more strongly than any other anion. Chloride is bound much more tightly by the $n = 8$ host, but there is not a particularly large decrease in equilibrium constant as n increases. This is in contrast to the pronounced specificity often seen in cation binding Lewis base macrocycle chemistry. Another problematic aspect of anion inclusion by the bidentate tin macrocycles is that the equilibrium constants are, at best, equal to, and in most cases, less than the equilibrium constant for the simple addition of halide ion to tributyltin halide.[5c,e] The only macrobicyclic tin host which has been shown to bind chloride to a substantially greater extent than Bu_3SnCl has four tin binding sites.[5e]

With this in mind, we began a theoretical study of anion binding by two classes of organoboron macrocycles. Class I is a series of macrobicyclic organoboranes with two bridgehead boron atoms. These macrobicycles are the boron analogs of the alkyltin compounds described above. One member of this series, diborabicycloundecane (I, $n = 3$) has been synthesized.[6a] Class II is a series of macrotricyclic hosts which contain four possible anion binding sites and are structurally related to the spherical macrotricycles of Lehn.[8]

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(1) (a) Hoechst Celanese. (b) Brooklyn College.

(2) (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Breuning, R. L. *Chem. Rev.* **1991**, *91*, 1721. (b) An, H.; Bradshaw, J. S.; Izatt, R. M. *Chem. Rev.* **1992**, *942*, 543. (c) Izatt, R. M.; Bradshaw, J. S.; Pawlak, K.; Breuning, R. L.; Tarbet, B. J. *Chem. Rev.* **1992**, *92*, 1261.

(3) Examples of such binding include the selective coordination of polyatomic anions by protonated macrocyclic polyamines. Anion binding by expanded protonated porphyrins and protonated porphyrin trimers has also been demonstrated. The latter example involves the surprising inclusion of polyoxoanions such as $PW_{12}O_{40}^{3-}$ in the large host cavity. An unusual anion inclusion complex involves two metal ions bound at opposite ends of a large tetraamino cryptand with a bridging azide ion between them: Lehn, J.-M.; Meric, R.; Vigneron, J.-P.; Bkouche-Waksman, I.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1991**, 62. Sessler, J. L.; Mody, T. D.; Ford, D. A.; Lynch, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 452. Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 947. Drew, M. G. B.; Hunter, J.; Marrs, D. J.; Nelson, J.; Harding, C. *J. Chem. Soc., Dalton Trans.* **1992**, 3235.

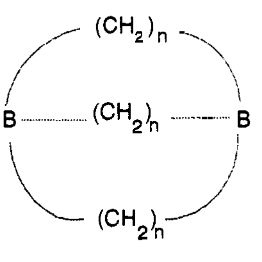
(4) (a) Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 193. (b) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 380. (c) Yang, X.; Johnson, S. E.; Khan, S. I.; Hawthorne, M. F. *Angew Chem., Int. Ed. Engl.* **1992**, *31*, 893. (d) Alsina, T.; Clegg, W.; Fraser, K. A.; Sola, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1010. (e) Simard, M.; Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 370.

(5) (a) Newcomb, M.; Horner, J. H.; Blanda, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 7878. (b) Newcomb, M.; Blanda, M. T. *Tetrahedron Lett.* **1988**, *29*, 4261. (c) Blanda, M. T.; Newcomb, M. *Tetrahedron Lett.* **1989**, *30*, 3501. (d) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294. (e) Blanda, M. T.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 4626. (f) Horner, J. H.; Squattrito, P. J.; McGuire, N.; Rickenspies, J. P.; Newcomb, M. *Organometallics* **1991**, *10*, 1741.

(6) (a) Greenwood, N. N.; Morris, J. H.; Wright, J. P. *J. Chem. Soc.* **1964**, 4753. (b) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063. (c) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420. (d) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (e) Katz, H. E. *Organometallics* **1987**, *6*, 1134. (f) Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179. (g) Feher, F. J.; Budzichowski, T. A.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5100.

(7) There is a quite unusual example of direct fluoride binding to a fluorinated macrocyclic polyether: Farnham, W. B.; Roe, D. C.; Dixon, D. A.; Calabrese, J. C.; Harlow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 7707.

0002-7863/93/1515-11216$04.00/0



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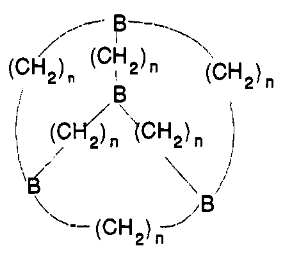

II

Table I. Trimethylboron and Its Anion Complexes: Summary of Computational Results

	$(CH_3)_3$-B	$(CH_3)_3$-BH^-	$(CH_3)_3$-BF^-	$(CH_3)_3$-BCl^-	$(CH_3)_3$-BO^{2-}
B–L (Å)		1.22	1.37	1.91	1.34
B–C (Å)	1.54	1.58	1.60	1.57	1.63
C–B–C (deg)	120.0	109.4	108.8	111.8	103.8
binding energy[a] (kcal/mol)		–51.2	–44.1	–15.2	–154.0

[a] Defined as the standard enthalpy of reaction for $(CH_3)_3B + X^{n-} \rightarrow (CH_3)_3BX^{n-}$. Enthalpies of formation for neutral trimethylboron and its complexes were computed with AM1, while the enthalpies of formation of the gas-phase anions were taken from the literature (refs 18–21).

The chemistry of multidentate Lewis acid macrocycles ("anti-crown" chemistry[4a]) is inverse to that of the usual Lewis base macrocycles, such as in cryptand and crown ether chemistry. While highly specific cation recognition has been clearly demonstrated, and is a continuing goal of Lewis base macrocycle chemistry,[2a] the design of anion-specific Lewis acid macrocycles is a parallel and equally important objective. In order to study the extent to which multidentate Lewis acid macrocycles can exhibit selective anion binding, we have completed quantum mechanics calculations on the class I and class II macrocycles and their inclusion complexes with H^-, F^-, Cl^-, and O^{2-}. These calculations were designed to elucidate the structure of the above macrocycles, as well as the factors that contribute to the anion recognition process.

Computation Methods

Computer-generated molecular models can aid in understanding complex chemical phenomena by determining the three-dimensional atomic structure and internal molecular energies,[9] as well as by providing detailed visualization of many electronic and structural features of the system of interest. Molecular modeling techniques are based on relationships that define the internal molecular energy as a function of atomic coordinates. The three-dimensional structure is computed by minimizing the internal molecular energy while the dynamic behavior can be simulated by incorporating this internal energy into Newton's equations of motion. This internal energy can be represented in two ways: (1) as a sum of classical forces that correspond to the types of motion or interactions associated with molecular systems (i.e., bond stretching, bond bending, torsional bond rotation, electrostatic interactions, etc.) or (2) as an approximate solution of Schrődinger's equation. Simulations utilizing the first representation are termed force field calculations and are described in detail elsewhere.[10] Quantum mechanics calculations, however, fall into several different categories, depending on the level of parameterization used in the energy solution. We have chosen the AM1 semi-empirical method for studies reported here. This method is briefly described below.

(a) AM1 Calculations. AM1 is a molecular orbital method which has been shown to give reliable bond lengths, bond angles, and gas-phase standard enthalpies of formation for normal-valent compounds. The requisite parameters are found in the literature.[11,12] As summarized in a recent review[13] of various computational methods, a critical examination of the results of AM1 calculations gives average absolute errors of 0.050 Å for bond lengths and 3.3° for bond angles.[14] Gas-phase standard enthalpies of formation are shown[15] to have an absolute error of 9.6 kcal/mol for normal-valent compounds. Results for hypervalent compounds are considerably less reliable.

(b) Modeling Scheme. Molecular modeling of the class I and class II boron macrocycles begins with the determination of an approximate three-dimensional structure. Molecular graphics and force field methods contained within the CHEMLAB[16] molecular modeling system were used to obtain these initial molecular geometries. The resulting structures were then optimized using AM1 semi-empirical quantum mechanics contained within the MOPAC 6.0[17] computer program, yielding both structural information and gas-phase standard enthalpies for each neutral macrocycle. Structures and enthalpies of formation for the complexed anions were determined by placing an H, F, Cl, or O atom at the center of the optimized neutral macrocycle and again optimizing with AM1 quantum mechanics specifying the appropriate anion charge. It should be noted that these calculations do not include any effect of solvation.

Results

In the accompanying tables, we report selected bond lengths, bond angles, and binding energies computed for the various species. In all cases, the reported binding energy is defined as the standard enthalpy change for the reaction of the neutral organoboron compound with the anion to yield the anion complex. The standard enthalpies of formation of the neutral host and the anion complexes were computed, while the standard enthalpies of formation of hydride (+33.2 kcal/mol),[18] fluoride (–59.9 kcal/mol),[19] chloride (–55.9 kcal/mol),[20] and oxide (+231 kcal/mol)[21] were taken from standard sources. The least well established of these values is oxide. Values for fluoride and chloride were chosen particularly to allow direct comparison of our results with recent experimental work.[22]

(a) Trimethyl Boron and Its Anion Complexes. The results of calculations on $(CH_3)_3B$ and its anion complexes with H^-, F^-, Cl^-, and O^{2-} are presented in Table I. The calculated standard enthalpy of formation (–24.5 kcal/mol) and the geometric parameters for $(CH_3)_3B$ (Table I) are in nearly exact agreement with the original AM1 results of Dewar.[12] The most commonly cited[23] experimental value for the enthalpy of formation is –29.3 ± 5.5 kcal/mol. Although a recent theoretical study[24] yielded a value of –29.19 kcal/mol, the AM1 value is certainly acceptable given the reported experimental error and the acknowledged limits[13–15] of AM1. An experimental study[22] of fluoride and chloride affinities of many Lewis acids gives a binding energy of –47.2 kcal/mol for the addition of fluoride to $(CH_3)_3B$. Our calculated value is –44.1 kcal/mol. Additional calculations were

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(8) Graf, E.; Kintzinger, J. P.; Lehn, J.-M.; LeMoigne, J. *J. Am. Chem. Soc.* **1982**, *104*, 1672.

(9) Jacobson, S. H.; Pearlstein, R. A.; Hopfinger, A. J.; Tripathy, S. K.; Orchard, B.; Potenzone, R.; Doherty, D.; Grigoras, S. *Sci. Comput. Automat.* **1984**, *1*.

(10) Burkert, U., Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(11) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(12) Dewar, M. J. S.; Jie, C.; Zoebisch, E. G. *Organometallics* **1988**, *7*, 513.

(13) Levine, I. N. *Quantum Chemistry*, 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1991; Chapter 17.

(14) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(15) Stewart, J. J. P. *J. Comput. Chem.* **1990**, *11*, 543.

(16) CHEMLAB program obtained from Molecular Design Ltd., 2132 Farallon Drive, San Leandro, CA.

(17) QCPE program 506 by the Dewar research group and J. J. P. Stewart. Obtained from QCPE, Indiana University, Bloomington, IN.

(18) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl.* **1982**, *11*.

(19) Woolf, A. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 1.

(20) Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1975**, *4*, 1.

(21) Karapet'yants, M. Kh.; Karapet'yants, M. K. *Handbook of Thermodynamic Constants of Inorganic and Organic Compounds*; Ann Arbor-Humphrey Science Publishers: Ann Arbor, London, 1970.

(22) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

(23) (a) Cox, J. D.; Pilcher, D. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. (b) Murphy, M. K.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 2437. (c) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433.

(24) Sana, M.; Leroy, G.; Wilante, C. *Organometallics* **1991**, *10*, 264.

Table II. Ion Binding Energies (kcal/mol) for Anion Complexes with $B_2[(CH_2)_n]_3$

n	H^-	F^-	Cl^-	O^{2-}
3	–42.6	61.3	47.7	–136.8
4	–75.5	–63.0	53.9	–217.1
5	–76.0	–78.9	25.3	–245.0
6	–78.6	–88.3	–10.8	–256.7
8	–63.9	–51.0	–13.2	–237.0
10	–61.8	–51.0	–12.1	–233.8

Table III. Computed Geometric Parameters for $B_2[(CH_2)_n]_3$ and Its Anion Complexes[a]

B1–B2 Distance (Å)

n	B2C*n*	B2C*n*H⁻	B2C*n*F⁻	B2C*n*Cl⁻	B2C*n*O²⁻
3	2.53	2.47			
4	2.89	2.55	2.73		2.55
5	3.80	2.69	2.75		2.68
6	4.16	2.74	2.77	3.96	2.74
8	5.55	5.12	5.00	5.11	2.75
10	6.81	5.70	6.17	5.93	2.74

B1–X and X–B2 Distances (Å)

n	B2C*n*H⁻	B2C*n*F⁻	B2C*n*Cl⁻	B2C*n*O²⁻
3	1.24/1.24			
4	1.28/1.28	1.36/1.37		1.40/1.41
5	1.34/1.35	1.38/1.38		1.41/1.41
6	1.36/1.38	1.38/1.38	1.99/2.00	1.43/1.44
8	1.22/3.92	1.36/3.68	1.91/3.25	1.45/1.46
10	1.22/4.85	1.37/5.07	1.89/4.11	1.45/1.45

B–X–B Angles for μ–X Complexes (deg)

n	B2C*n*H⁻	B2C*n*F⁻	B2C*n*Cl⁻	B2C*n*O²⁻
3	173.3			
4	169.6	178.6		130.1
5	174.0	174.0		142.0
6	177.6	178.2	165.7	145.2
8				142.1
10				141.5

Average C–B1–C & C–B2–C Angles (deg)

n	B2C*n*H⁻	B2C*n*F⁻	B2C*n*Cl⁻	B2C*n*O²⁻
3	119.7/119.8			
4	116.1/116.4	114.4/114.4		113.0/113.5
5	110.1/110.9	109.5/109.7		107.6/108.3
6	108.5/110.3	107.5/108.6	114.6/115.5	105.0/107.0
8	110.6/119.9	108.7/119.7	112.8/119.4	103.7/104.3
10	110.2/119.8	108.5/119.9	109.6/119.9	103.4/104.2

[a] Geometric parameters are only listed for stable anion complexes.

done on $(C_2H_5)_3B$ and its complexes with F^- and Cl^- in order to compare our results with experimental values.[22] The calculated binding energy for F^- is –49.0 kcal/mol which is in excellent agreement with the experimental value (–51.0 kcal/mol). The excellent agreement between our calculations and the reported experimental results for fluoride binding provides validation of the computational method. Although our value for Cl^- binding (–17.6 kcal/mol) is not as close to the experimental value (–23.8 kcal/mol), the two values are within the error limits of the respective determinations.

Of the anion complexes studied, we find that oxide exhibits the strongest binding energy. This is due in part, however, to the highly endothermic heat of formation for oxide itself. Hydride and fluoride are found to bind to about the same extent, while chloride was found to have the lowest binding energy. This weak chloride binding has been observed experimentally. For example, the binding energy for F^- with most Lewis acids is 2–3 times greater than the Cl^- binding energy.[22] The strength of anion–host binding can also be described by changes in the boron geometric parameters. Trimethylboron by itself is trigonal planar (D_{3h}), and the boron atom is sp^2 hybridized. Anion addition produces trigonal pyramidal (C_{3v}) complexes in which the boron is of approximate sp^3 hybridization. The boron–carbon bond length in $(CH_3)_3B$ is increased by as much as 0.09 Å on anion addition. This calculated increase in bond length is consistent with experimental results. For example, the boron–oxygen bond length in $B(OH)_3$ is about 0.1 Å less[25] than that in $B(OH)_4^-$. From the data in Table I, it can be seen that the more strongly the anion is bound, the longer the C–B bond length becomes. Additionally, we find an accompanying change in the C–B–C angle. As anion binding energy increases, the C–B–C angle becomes more acute. These structural and thermodynamic results for $(CH_3)_3B$ and its anion complexes provide a framework for the discussion of the anion inclusion complexes formed with the class I and class II macrocycle hosts.

(b) $B_2[(CH_2)_n]_3$ and the Anion Complexes. Calculations were done on $B_2[(CH_2)_n]_3$ for *n* = 2–6, 8, 10. The *n* = 2 system, however, is too small to allow planarity at the bridgehead. The strain which results in a slight exo pyramidalization of the borons produces a standard enthalpy of formation which is endothermic. Therefore, this system was not considered further. The reactions of each one of the other organoboron macrobicycles were studied with H^-, F^-, Cl^-, and O^{2-}. Ion binding energies for the anion complexes of $B_2[(CH_2)_n]_3$ are presented in Table II. Selected structural parameters for the various $B_2[(CH_2)_n]_3$ macrobicycles and their anion complexes are presented in Table III. Since the macrobicycles studied here all contain three B–B linkages of equal length (the same value of *n*), an abbreviated notation is used to identify the various complexes. The notation indicates the number of bridgehead boron atoms and the number of carbon atoms in each B–B linkage. For example, $B_2[(CH_2)_4]_3$ is denoted B2C4 and its hydride inclusion complex is B2C4H.

The ion binding energies (Table II) generally display some dependence on cavity size. For example, the B2C*n*H inclusion complexes show the strongest binding energies for *n* = 4–6. The B2C3H complex has the smallest H^- binding energy, and it also maintains the planarity of both bridgehead borons. The *n* = 4–6 series allows for increasing pyramidalization at both bridgeheads. Here, H^- forms a nearly linear symmetrical bridge between the two boron atoms of the macrobicycle, a μ-H system.[26] As *n* increases, the B–H bond distances also increase. For *n* greater than 6, μ-H binding does not occur and the hydride binds to only one boron. One bridgehead boron is now sp^3 with a normal B–H bond length, and the other is sp^2 hybridized.

Examination of the molecular geometries of the series of fluoride and chloride complexes (Table III) reveals that the trends in bond length and boron hybridization are similar to trends observed for hydride inclusion complexes. A common structural feature in all systems is that anion inclusion results in a decrease in the B–B distance.[27] Fluoride inclusion complexes show the greatest binding energies for B2C5F and B2C6F, while the most stable chloride inclusion complexes involve larger cavities. B2C6Cl is the smallest cavity able to contain a chloride ion. Some size selectivity is apparent from these calculations, but generally, the change in binding energy for increasingly larger cavities is not particularly dramatic. It is interesting that B2C6Cl and B2C8Cl have almost identical binding energies, but very different modes of binding. B2C6Cl has a μ-Cl structure while B2C8Cl is unbridged. Moreover, the binding energy of the inclusion complex

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(25) Christ, C. L.; Clark, J. R.; Evans, H. T. *Acta Crystallogr.* **1958**, *11*, 761.

(26) Although several B–H–B angles in H^- inclusion complexes of bidentate organoborane ligands are generally bent (see ref 5), theoretical calculations (see ref 31) on $B_2H_7^-$ predict very small energy differences among the various alternative geometries about the bridging hydride. While there is nothing unusual in the near linear B–X–B bridge bonds in the B2C*n*X complexes, bent structures are not expected to differ significantly in energy.

(27) Calculations on B2C3F, B2C5Cl, and B2C3O all show increases in B–B bond length on anion inclusion and endothermic ion binding energies. In each case the ligand is too small to permit successful inclusion of a relatively large anion.

Table IV. Ion Binding Energies (kcal/mol) for Anion Complexes with $B_4[(CH_2)_n]_6$

n	H^-	F^-	Cl^-	O^{2-}
2	−76.9	−60.6	19.0	−332.0
3	−62.1	−77.1	−29.8	−289.7
4	−61.8	−53.3	−16.7	−267.3

is slightly less than that for simple chloride addition to $(CH_3)_3B$. On the other hand, stable hydride and fluoride inclusion complexes have binding energies which are greater than the binding energy for anion addition to $(CH_3)_3B$.

The most dramatic example of the effect of anion inclusion on the boron–boron distance is found in the B2CnO series of inclusion complexes. Here, such strong boron–oxygen bonds are formed that even B2C10O contains a symmetrical B–O–B bridge. The B–B distance in B2C10 (6.81 Å) is more than halved on O^{2-} inclusion to form B2C10O (2.74 Å). Aside from the least stable B2C4O complex, the binding energies and structural parameters are very similar for the series B2C5O–B2C10O. These μ-O complexes all contain a bent B–O–B linkage with an average bond angle slightly less than 143°. The binding energies of the μ-O complexes are significantly greater than those for simple oxide addition to $(CH_3)_3B$.

(c) $B_4[(CH_2)_n]_6$ and the Anion Complexes. Calculations were done on $B_4[(CH_2)_n]_6$ for n = 2–4 and also on the inclusion complexes of these three macrotricycles with H^-, F^-, Cl^-, and O^{2-}. Binding energies for the various anion inclusion complexes are contained in Table IV, and selected structural parameters are collected in Table V. Following an abbreviated notation similar to that used in the last section, B4C3 denotes $B_4[(CH_2)_3]_6$ and B4C3X represents its various anion complexes.

The structures of both the neutral macrotricycles and their anion complexes are most easily discussed in terms of the local symmetry of the four boron atoms, which we shall call the B4 unit. In B4C2, the B4 unit is of almost perfect tetrahedral (T_d) symmetry. The average B–B distance is 3.05 Å (standard deviation = 0.06 Å). This corresponds to a tetrahedron in which the distance from the center to any boron atom is 1.86 Å. B4C3 is also approximately T_d with an average B–B distance of 4.03 Å. Here, the center to boron distance is 2.46 Å. The very large B4C4 cage has an average B–B distance of 4.97 Å (standard deviation = 0.38 Å) and a center to boron distance of 3.03 Å. As the macrotricycles increase in size, the symmetry designations become increasingly approximate (as shown by the larger standard deviations), but they provide a very useful frame of reference for discussion and reporting of the complex molecular geometries. All four borons in every neutral macrotricycle are sp^2 hybridized.

Two anion inclusion complexes retain the T_d local symmetry. B4C2O and B4C3O contain μ_4-O atoms. The local symmetry is reduced to C_{2v} when the included anion forms a B–X–B bridge along one edge of the B4 tetrahedron. This has the effect of shortening one B–B distance relative to the other five such distances. Such μ-X linkages are found in B4C2H, B4C2F, B4C3F, and B4C4O. Anions in relatively large cavities cannot bridge even two borons, and a covalent bond is formed with just one boron. This reduces the local (B4 unit) symmetry to C_{3v}. As a consequence of the inward pyramidalization of the apical boron, the apical B–B distances are shortened with respect to the three B–B distances in the basal plane. Examples of this symmetry are found in B4C3H, B4C4H, B4C4F, and B4C4Cl. The last remaining anion complex is B4C3Cl, and it is of C_{3v} local symmetry. It differs from the other four C_{3v} complexes in that the chloride is a μ_3-Cl; it bridges the three borons in the basal plane, and this shortens these three B–B distances compared with the distances to the apical boron. The B4C3X complexes display all four modes of binding: B4C3H is unbridged (C_{3v}), B4C3F is a μ-F complex (C_{2v}), B4C3Cl is a μ_3-Cl complex (C_3v), and B4C3O has a μ_4 bridging oxide (T_d). Once again we note that the symmetries of the bridges in the anion complexes, reported above, are somewhat approximate but are used here for purposes of conceptualization.

As in the case of the B2CnX series, stable B4CnX complexes involve rehybridization of one or more borons, and a general decrease in B–B distances.[28] The strongest binding energies of chloride and oxide in B4Cn hosts, however, are substantially greater than the strongest binding in the B2Cn series. This enhanced anion binding occurs for cases in which the included anion binds to more than two boron atoms. The binding energies of hydride and fluoride are similar to the binding in the B2CnX complexes because these anions bind to at most two borons in either class I or class II host macrocycles.

Discussion

(a) Size Selectivity. If one compares just the H^-, F^-, and Cl^- inclusion complexes of the B2Cn series of ligands, it is apparent that some size selectivity exists. H^- can fit into the $n \geq 3$ cavities, F^- fits into $n \geq 4$, and Cl^- fits into cavities with $n \geq 6$. For F^- and Cl^- this selectivity is exactly parallel to that observed experimentally[5b,e] in the $ClSn[(CH_2)_n]_3SnCl$ systems. The most stable organotin inclusion complexes of F^- and Cl^-, however, involve larger hosts (greater n) compared to those in the B2Cn boron complexes, reflecting the longer Sn–X bond distance (compared to the B–X distance).

It is significant that the size selectivity is not based on the ionic radii of the included anions. In terms of ionic radii, H^- is larger[29] than F^-, but H^- can fit into a smaller cavity. The reason for this is that the interaction between boron and an included anion is more accurately described in terms of the formation of covalent bonds rather than purely ionic interactions. A significant amount of charge transfer from the anion to the host occurs upon complex formation. Mulliken charge distribution analysis shows partial atomic charges of approximately −0.12, −0.27, −0.39, and −0.50 for H^-, F^-, Cl^-, and O^{2-}, respectively. An interesting consequence of this is that anions can fit into cavities which are smaller than themselves. For example, the B–B distance in B2C3 is less than the ionic diameter of H^-, but nevertheless, B2C3H has an exothermic binding energy.

Although B2C3H is stable, it is not as stable as larger B2CnH complexes because the relatively large H^- anion does not permit much rehybridization of the boron atoms and the B–H distance is shorter than the optimum B–H distance found in μ-H systems. Various experimental values for B–H distances in μ-H systems[6b,d] are approximately 1.3 Å, in good agreement with our value for the most stable μ-H B2CnH complex, n = 6. Indeed, we find that except for those containing Cl^- the most stable inclusion complexes involve μ bridges, and the optimum host geometry will allow μ-X formation. This occurs in the B2Cn system at n = 6 for H^-, F^-, and O^{2-}.

Turning now to the B4Cn series, the computed binding energies in Table IV show that H^- and O^{2-} are complexed best by B4C2. B4C2H has a μ-H structure, and the binding energy is virtually the same as that in B2CnH with n = 4–6. B4C3H and B4C4H are unbridged, and the decrease in binding energy compared to that for the n = 2 host is exactly parallel to that observed in the B2CnH series when n was increased beyond the size which would allow μ-H bridge formation. O^{2-} also prefers the n = 2 in the B4Cn series of hosts, but, in this case, there is a much more favorable binding energy compared to that for the B2Cn hosts because the included oxide interacts with all four borons. The decrease in binding energy as n increases is caused first by an increase in the B–O distance, for n = 3, and then by a change from μ_4-O to μ-O coordination for n = 4. In the latter case, the

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[28] B4C2 is too small to form a stable inclusion complex with chloride. Calculations on B4C2Cl show an increase in B–B distance, relative to B4C2, and an endothermic binding energy (+19.0 kcal/mol).

[29] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Table V. Computed Geometrical Parameters for $B_4[(CH_2)_n]_6$ Anion Complexes

species	B4 unit symmetry[a]	average B–B distance[b] (Å)	average C–B–C angles[c] (deg)	average B–X distance[d] (Å)	average B–X–B angle[e] (deg)
B4C2	T_d	3.05(6)	119.4(4)		
B4C2H	C_{2v}	2.91(5)/2.35(1)	115.0(2)/119.8(2)	1.36(2)	119.3(1)
B4C2F	C_{2v}	2.89(5)/2.46(1)	119.5(2)/113.8(2)	1.42(2)	119.4(1)
B4C2O	T_d	2.66(6)	115.0(4)	1.63(4)	109.5(6)
B4C3	T_d	4.03(6)	119.8(4)		
B4C3H	C_{3v}	4.09(3)/3.49(3)	119.4(3)/109.5(1)	1.22(1)	
B4C3F	C_{2v}	3.86(5)/2.58(1)	119.7(2)/108.4(2)	1.39(2)	136.0(1)
B4C3Cl	C_{3v}	3.81(3)/3.44(3)	119.3(1)/114.0(3)	2.05(3)	113.8(3)
B4C3O	T_d	2.82(6)	107.1(4)	1.72(4)	109.4(6)
B4C4	T_d	4.97(6)	120.0(4)		
B4C4H	C_{3v}	4.98(3)/4.63(3)	120.0(3)/110.1(1)	1.23(1)	
B4C4F	C_{3v}	5.02(3)/4.51(3)	119.9(3)/108.2(1)	1.36(1)	
B4C4Cl	C_{3v}	5.02(3)/4.55(3)	119.7(3)/115.0(1)	1.91(1)	
B4C4O	C_{2v}	4.48(5)/2.62(1)	119.6(2)/107.2(2)	1.45(2)	128.2(1)

[a] Approximate local symmetry of the B4 unit. [b] The number in parentheses indicates the number of equivalent B–B distances which are averaged. [c] The number in parenthese indicates the number of equivalent C–B–C angles which are averaged. [d] Average B–X distances are given for borons which are interacting (bonding) with the anion. The number in parentheses is the number of B–X lengths which are averaged. All of the bridges are approximately symmetrical. [e] The number in parentheses refers to the number of B–X–B angles which are averaged. Averages are given for borons which form bridges with the anion.

structure and binding energy are similar to those found in the B2C*n*O series.

F^- and Cl^- prefer binding to B4C3. In the latter case, the large chloride ion does not fit into the B4C2 cavity. More importantly, B4C3Cl forms a μ_3-Cl structure which has a more favorable binding energy than any B2C*n*Cl complex. B4C4Cl is a μ-Cl complex with a binding energy very similar to that for B2C6Cl. Thus, size selectivity is apparent for chloride binding: the $n = 2$ host is too small to allow binding at all, and the $n = 4$ host is too large to allow the more stable μ_3-Cl bridge structure. Although B4C2F and B4C3F both form μ-F structures, F^- ion binding is weaker in the B4C2F case. This is attributed to some steric interference in the smaller B4C2 host. Similar behavior was found in the B2C4F complex. In both cases the average C–B–C bond angles (of the coordinated borons) are about 114° and the B–F bond lengths are identical. The larger B4C3 host has the optimum size to form the μ-F complex and thus exhibits the strongest ion binding. Again, this is completely analogous to the B2C6F complex. In the B4C4F complex, F^- is bound to only one boron, and this reduces the binding energy, as has been pointed out for the B2C*n* series. Although the B–F–B angles are considerably more acute in the B4C*n*F complexes, this does not have an effect on anion binding energies. Thus, the B4 and the B2 systems may be considered quite similar for fluoride binding. Both hosts exhibit some size selectivity based on an optimum cage size for μ-F bridge formation. Binding energy is reduced in small cages due to steric interference and in large cages due to the ion being bound to only one boron.

(b) Lack of Ligand Specificity in $B_2[(CH_2)_n]_3$ Anion Complexes. In contrast to cation macrocycle chemistry, which usually exhibits significant ligand specificity, a number of B2C*n* ligands have comparable binding energies with the same anion. This effect is also seen for hydride binding in the B4C*n* series for $n = 3$ and $n = 4$, but lack of ligand specificity is most clearly demonstrated by our results for B2C*n* hosts and their anion inclusion complexes. Therefore, this discussion will focus on our results for anion binding to the class I macrocycles, B2C*n*. For hydride, as *n* increases from 4 to 6 the B–H bond lengths increase and the hybridization of the bridgehead borons has increasing sp^3 character. The increase in bond length tends to make the binding energy less favorable, while the increasing sp^3 character tends to make the complex more stable. These opposing factors result in relatively constant binding energy for *n* between 4 and 6. A similar pattern is observed for fluoride complexes. As *n* increases beyond 6, the host cavity becomes too large for μ-X bridging and the included anion then binds to only one bridgehead boron. This results in decreases in binding energy of 14.7 and 37.3 kcal/mol for H^- and F^-, respectively.

Oxide complexes exhibit a relatively constant binding energy for *n* between 4 and 10. Here, the B2C*n*O complexes exhibit increasing sp^3 character as *n* increases from 4 to 6, similar to the case for B2C*n*F and B2C*n*H complexes. However, unlike the case for B2C*n*F and B2C*n*H complexes, μ-O bridging was observed in all of the B2C*n*O complexes studied due to very strong boron–oxygen interactions. The B–O–B linkage is so strong, in fact, that the binding energies of the B2C*n*O complexes are all greater than the binding energy for simple addition to $(CH_3)_3B$. B2C4O has the least favorable binding energy because it has the smallest hybridization change of the bridgehead borons and the most acute B–O–B angle, which are both consequences of the small cavity size. All of the other B2C*n*O complexes have similar B–O bond lengths and B–O–B angles.[30] A slight decrease in binding energy was observed for $n > 6$ because maintaining the μ-O bridge in the larger host macrocycles results in a considerably deformed cage structure compared to that for the equilibrium neutral macrocycle. The larger B2C*n* macrocycles, however, are relatively flexible, so the change in energy upon going from $n = 6$ to $n = 10$ is not great, and as a consequence, no particular B2C*n* ligand is specific for O^{2-}.

In contrast to binding of the other anions studied, chloride binding shows no preference for μ-Cl formation. The binding energy is virtually unchanged in going from bridged to unbridged structures. A very small increase in binding energy is observed as *n* increases from 6 to 10. This is attributed to the extra stabilization acquired from distribution of the anionic charge over a larger host. Thus, again, but for different reasons than the case for H^-, F^-, and O^{2-}, more than one member of the B2C*n*Cl series exhibit similar binding energies, and well-defined ligand specificity is not observed. This lack of ligand specificity is also found experimentally in organotin inclusion complexes.[5] Another interesting experimental result in the organotin chloride complexes is that rapid chloride exchange ("chloride jump") is observed.[5a,e] The similar binding energies for bridged and unbridged chloride inclusion complexes found here suggest that the transition state for chloride exchange in organotin complexes may be reasonably low in energy, resulting in facile exchange. A similar result is predicted for B2C8Cl.

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(30) The decidedly nonlinear μ-O bridges have angles somewhat larger than the B–O–B angles observed in crystalline borates, and the B–O bond lengths are slightly longer: Corazza, E.; Menchetti, S.; Sabelli, C. *Acta Crystallogr.* **1975**, *B31*, 1993.

(31) (a) Raghavachari, K.; Schleyer, P. v. R.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 5917. (b) Sapse, A. M.; Osorio, L. *Inorg. Chem.* **1984**, *23*, 627. (c) see also ref 12.

(c) Ligand Rigidity in $B_4[(CH_2)_n]_6$. The nature of the anion binding process in boron-containing macrocycles is such that anion inclusion occurs with a decrease in B–B distance which is caused by a rehybridization of the boron atoms. This rehybridization can occur only if the ligand is sufficiently flexible to accommodate the requisite conformational change. While this flexibility was seen in B2C*n* hosts, the B4C*n* hosts appear to be considerably more rigid. B4C2 is the most rigid of the B4C*n* ligands. This is clearly demonstrated by its almost perfect T_d symmetry, and the fact that in B4C2O the borons undergo only a slight rehybridization even though the B–O distance is quite elongated compared to B–O distances in the B2C*n*O complexes (i.e., the bridgehead boron atoms remain nearly planar due to macrocycle rigidity, not boron–anion steric interference as was the case in some of the B2C3X complexes). The larger B4C3 macrocycle is slightly more flexible near the bridgehead borons, and allows considerably greater boron rehybridization, but is still overall relatively rigid and results in even longer B–O distances. This causes a less favorable binding energy for oxide compared to B4C2O. As *n* is increased once more to 4, cage rigidity is again demonstrated because here the μ_4-O bridge is not maintained. This behavior should be compared to that for the more flexible B2C*n* hosts which allow μ-O bridges for all *n*. It is interesting to note that although the B4C*n* hosts are more rigid than the B2C*n* hosts, and the B–O distances are quite a bit elongated compared to the distances observed in the B2C*n* series, the binding energy is considerably greater for the B4C*n*O complexes.

Summary

Molecular orbital (AM1) calculations were performed on trimethylboron, two classes of boron-containing macrocycles, and their anion complexes with H^-, F^-, Cl^-, and O^{2-}. These calculations indicate that ion binding occurs with a change in boron hybridization from sp^2 to sp^3. The nature of the anion–boron interaction was found to be more like a covalent bond than a purely ionic interaction. A significant amount of charge is transferred from the anion to the host upon complexation. An important consequence of this is that anions can fit into cavities which are smaller than their ionic diameters. Size exclusion, μ-X bridge formation, and cage flexibility are all key factors for anion complex formation. In both class I and class II hosts, size exclusion was observed (i.e., there was a minimum cage size which would allow ion binding to occur). Formation of a μ-X bridge was found to improve ion binding. This effect was particularly dramatic for oxide and least prevalent for chloride. Oxide and chloride form μ_4-O and μ_3-Cl bridges with class II macrocycles, which significantly improve their binding affinity. Fluoride and hydride, however, only exhibit μ-X bridge formation (i.e., the anion is bound to only two boron atoms) even with the B4C*n* series of hosts. Thus, hosts designed to bind oxide or chloride more tightly and with greater specificity should contain at least four Lewis acid sites. Increased host flexibility facilitates μ-X bridging, but this simultaneously decreases ligand specificity. Class I macrocycles were found to be considerably more flexible than class II hosts. The results of this study suggest that it may be possible to design different Lewis acid macrocycle hosts for optimum binding with specific anions.

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