Boric acid adsorption on humic acids: *Ab initio* calculation of structures, stabilities, ^{11}B NMR and ^{11}B,^{10}B isotopic fractionations of surface complexes

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Abstract

Boric acid, $B(OH)_3$, forms complexes in aqueous solution with a number of bidentate O-containing ligands, HL^-, where H_2L is $C_2O_4H_2$ (oxalic acid), $C_3O_4H_4$ (malonic acid), $C_2H_6O_2$ (ethylene glycol), $C_6H_6O_2$ (catechol), $C_{10}H_8O_2$ (dioxynaphthalene) and $C_2O_3H_4$ (glycolic acid). McElligott and Byrne [McElligott, S., Byrne, R.H., 1998. Interaction of $B(OH)_3^0$ and HCO_3^- in seawater: Formation of $B(OH)_2CO_3^-$. *Aquat. Geochem.* 3, 345–356.] have also found $B(OH)_3$ to form an aqueous complex with HCO_3^{-1}. Recently Lemarchand et al. [Lemarchand, E., Schott, J., Gaillardeet, J., 2005. Boron isotopic fractionation related to boron sorption on humic acid and the structure of surface complexes formed. *Geochim. Cosmochim. Acta* **69**, 3519–3533] have studied the formation of surface complexes of $B(OH)_3$ on humic acid, determining ^{11}B NMR shifts and fitted values of formation constants, and ^{11}B, ^{10}B isotope fractionations for a number of surface complexation models. Their work helps to clarify both the nature of the interaction of boric acid with the functional groups in humic acid and the nature of some of these coordinating sites on the humic acid. The determination of isotope fractionations may be seen as a form of vibrational spectroscopy, using the fractionating element as a local probe of the vibrational spectrum. We have calculated quantum mechanically the structures, stabilities, vibrational spectra, ^{11}B NMR spectra and ^{11}B,^{10}B isotope fractionations of a number of complexes $B(OH)_2L^-$ formed by reactions of the type:

$$B(OH)_3 + HL^- \Rightarrow B(OH)_2L^- + H_2O$$
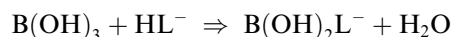
using a 6-311G(d,p) basis set and the B3LYP method for determination of structures, vibrational frequencies and isotopic fractionations, the highly accurate Complete Basis Set-QB3 method for calculating the free energies and the GIAO HF method with a 6-311+G(2d,p) basis for the NMR shieldings. The calculations indicate that oxalic acid, malonic acid, catechol and glycolic acid all form stable complexes ($\Delta G < 0$ for Reaction (1)),which are deshielded (less negative δ) vs. the $(C_2H_5)_2OBF_3$ reference by 3.6, 1.5, 6.5 and 5.4 ppm, respectively, and which are isotopically lighter than $B(OH)_4^-$ (more negative δ 11B) by 3‰, 2‰, 5‰ and 2‰, respectively. The calculated ^{11}B NMR shifts match well literature values and with the results of Lemarchand et al. (2005), while the calculated isotopic fractionations are also consistent with their results, but show much smaller deviations from $B(OH)_4^{-t}$ than indicated by these authors. This is a consequence of the use by Lemarchand et al. (2005) of a value of 1.0194 [Kakihana, H., Kotake, M., Satoh, S., Nomura, M., Okamoto, M., 1977. Fundamental studies on the ion-exchange separation of boron isotopes. *Bull. Chem. Soc. Jpn.* **50**, 158–163.] for the ^{11}B,^{10}B isotopic exchange equilibrium constant of the $B(OH)_3$, $B(OH)_4^-$ pair which is obsolete and should be replaced by the new purely experimentally determined value of 1.0285 for 0.63 molar ionic strength [Byrne, R.H., Yao, W., Klochko, K., Kaufman, A.J., Tossell, J.A., 2006. Experimental evaluation of the isotopic exchange equilibrium $^{10}B(OH)_3 + ^{11}B(OH)_4^- = ^{11}B(OH)_3 + ^{10}B(OH)_4^-$ in aqueous solution. *Deep-Sea Res.* **1** (53), 684–688.] or 1.0308 for pure water [Klochko, K., Kaufman, A.J., Yao, W., Byrne, R.H., Tossell, J.A., 2006. Experimental measurement of boron isotope fractionation in seawater. *Earth Planet Sci. Lett.* **248**, 276–285]. Given this correction the $B(OH)_2L^-$ complexes are observed to be isotopically lighter than $B(OH)_4^-$ by only a few ‰. Changes in ^{11}B NMR shift and ^{11}B,^{10}B isotope fractionations for the $B(OH)_2L^-$ complexes, compared to $B(OH)_4^-$, are found to be correlated

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to some extent with distortions of the O–B–O angles from tetrahedral values and/or with B–O bond strength sums. Similar free energies for the corner-sharing and 4-ring isomers of $B(OH)_2CO_3^-$ suggest a mechanism for creation of both BIII and BIV environments when B is incorporated into calcite.

1. Introduction

To help in the characterization of a complex natural material it may often be useful to probe it with a succession of simple compounds which interact discretely with only certain parts of the material giving complexes with properties which are easy to measure and interpret. The adsorption of small molecules on discrete sites in zeolites and the spectroscopic characterization of changes in the properties of these molecules due to adsorption has become a valuable technique in zeolite chemistry (Klinowski, 1993; Bremard and Bougeard, 1995). For the case of many types of dissolved organic matter (DOM), such as humic acids, this general technique may also prove valuable. For example, a number of organic species adsorbed on humic acids have recently been characterized by NMR (Simpson, 2006). The trick is to find small molecule adsorbents which bind to only certain clearly designated sites in the humic acid and have properties which are easily measurable, characteristic of the adsorption site and readily interpretable.

A major fraction of DOM is composed of refractory humic compounds, polymers of variable composition (Morel and Hering, 1993). These substances are the most abundant C reservoir on Earth and play a significant role in a number of biogeochemical and environmental processes. Most relevant to the present study are their action as nutrient reservoirs for plants and as sorbents for toxic metal ions, radionuclides and organic pollutants. Although their overall structure is complicated and poorly defined, humic compounds appear to contain reasonably simple and consistent functional groups for coordination: principally carboxyl, alcohol and phenol. Progress has recently been made in characterizing their 3-D structure through atomistic modeling constrained by experimental data on elemental composition, density, spectra, etc. (Diallo et al., 2003). Titration of humic substances invariably produces broad graphs of increasing negative charge with increasing pH, which have been interpreted using both discrete site models (Lumsdon and Fraser, 2005) and continuous, electrostatically modified models (Milne et al., 2001). There may well be a range of 1st pK_a's in the humic acid sample and these pK_a's will be perturbed by the electrostatic environment created by the successive deprotonations (Trout and Kubicki, 2006). Studies of their UV–visible spectra also indicate substantial interactions between electron donor and acceptor groups within the humic acids (Del Vecchio and Blough, 2004). More detailed determination of specific sites of humic acids may be obtained using adsorbants which are neutral and which can bind to only those acid and alcohol sites with certain structural characteristics.

Recently, Lemarchand et al. (2005) have characterized carboxylic and phenolic sites in humic acid which strongly adsorb B-containing species, such as $B(OH)_3$. By measuring the total amount of adsorbed B it is then possible to assess surface complex binding constants, within a given model for the number of species present and their general characteristics. These parameters for such a model can be estimated from known complex formation constants in aqueous solution. They were also able to probe the ^{11}B NMR of the adsorbed species, which can readily give information on B coordination number and, with somewhat more care, provide some information on mid-range order about the B (e.g. Tossell, 1997; Zwanziger, 2005). Lemarchand et al. (2005) also determined the $^{11}B, ^{10}B$ isotopic distribution in the B adsorbed on the humic acid sample, and found that the adsorbed B was isotopically light compared to the $B(OH)_3$ species in solution. The $^{11}B, ^{10}B$ isotopic distribution is determined primarily by the vibrational spectrum of the material and may be considered a probe of that local part of this spectrum which can be perturbed by the substitution of ^{10}B for ^{11}B. In this respect, it may be more valuable and easier to interpret with respect to the local environment of the B than the full vibrational spectrum, which invariably depends upon geometric and electronic features both near to and far from the B atom.

Although the vibrational spectra of protonated and deprotonated humic acids have been determined (Lumsdon and Fraser, 2005), no IR studies of $B(OH)_3$ adsorption on humic acid have yet appeared. The adsorption of B-containing species on hydrous ferric oxide (Peak et al., 2003) and on hydrous ferric oxide and some other geomaterials (Su and Suarez, 1995) has been studied using reflection IR methods, but the focus has been on fairly weak adsorptions in which the borate vibrations are only slightly perturbed, rather than on reaction of B-containing species or their incorporation into the structure of the material.

If we make the assumption that reasonable estimates of all the interesting properties of boric acid–humic acid complexes can be obtained from their values for analogous aqueous solution complexes, then the quantum mechanical problem of calculating these properties becomes a manageable one. Calculations of ^{11}B NMR parameters for chemical compounds in the gas phase can now be done to quite high accuracy (Gauss and Stanton, 2002) although even Hartree–Fock level calculations are often quite accurate for calculating chemical shifts and distinguishing between different candidate structures for molecules (Cremer

et al., 1993). There has also been significant recent progress in calculating isotopic fractionation equilibrium constants from quantum chemical first principles (Oi, 2000; Schauble et al., 2004; Liu and Tossell, 2005; Tossell, 2005a). Similarly, accurate calculations of the vibrational spectra of small gas phase molecules, including accurate treatments of electron correlation and vibrational anharmonic effects are now common (Carbonniere et al., 2005). However, the inclusion of environmental effects on vibrational spectra still represents a considerable problem. Procedures are available which give qualitatively the correct change between gas phase and aqueous solution (Tomasi, 2004) but quantitative agreement is often still lacking. It is also possible to now calculate reaction free energies in solution (Tossell, 2003, 2005a,b) with near chemical accuracy (to within a few kcal/mol) for a number of different types of reactions, so long as the charge magnitudes of any ions are small, but the accuracy of the solution free energy is still limited by the accuracy of our methods for calculating hydration free energies.

In this study, we perform quantum mechanical calculations on a number of complexes formed by the condensation reaction of $B(OH)_3$, with various acid and alcohol anions, HL^-, giving complexes with the general formula $B(OH)_2L^-$, plus H_2O. The parent compounds of the ligands, H_2L, are oxalic acid, malonic acid, ethylene glycol, catechol, 1,8 dihydroxynaphthalene, acetic acid, and H_2CO_3. For each complex we have calculated the equilibrium geometry and the free energy difference of ^{11}B and ^{10}B isotopomers using a doubly polarized triple zeta basis set and the B3LYP HF-DFT hybrid method, the ^{11}B NMR shieldings with a triply polarized triple zeta basis and the HF method and (for the smaller complexes) the total free energy with the highly accurate composite Complete Basis Set-QB3 method (which uses the doubly polarized triple zeta B3LYP optimized geometry). All hydration free energies have been calculated using the conductor polarizable continuum method (CPCM). In addition to calculating these properties and comparing them with experiment we have examined correlations between the energetic and NMR properties and our calculated structural properties.

Our calculations of structures and vibrational spectra are at essentially the same quantum mechanical level as those in the recent study of Al^{3+} complexes of organic acids by Trout and Kubicki (2004). Trout and Kubicki (2006) have also addressed the question of the acidities of different sites on a model fulvic acid, using lower level quantum techniques for geometry optimization of the very complicated structures involved.

This study builds upon our previous work on the equilibrium constant for ^{11}B,^{10}B fractionation in the solute pair $B(OH)_3$, $B(OH)_4^-$ (Liu and Tossell, 2005). Direct experimental determinations of this equilibrium constant by measuring the difference of pK_a's of isotopically >99% enriched $^{10}B(OH)_3$ and $^{11}B(OH)_3$ crystalline boric acids (Byrne et al., 2006; Klochko et al., 2006) have yielded values for the equilibrium constant in the range 1.026–1.031, consistent with these calculations. We have also used quantum mechanical first principles to calculate the pK_a for $B(OH)_3$ and for several C and N containing oxyacids (Tossell, 2005b). The NMR calculations are similar to those used to assess speciation in B-containing boric oxide and borosilicate glasses (Tossell, 1997).

It is worthwhile to note that Pizer et al. (1995) have also calculated structures for a number of borate complex ions, like $B(OH)_2C_6H_4O_2^-$, using semiempirical molecular orbital methods. These studies were designed to help in the interpretation of their ^{11}B NMR and thermochemical results (Lorber and Pizer, 1976; Pizer and Ricatto, 1994). They found that such complexes contained a roughly tetrahedral, four-coordinate B, but with significant distance and angular distortions. The bonds to the OH groups were shorter (about 1.37–1.40 Å) and those to the O atoms in the L^{-2} group longer (about 1.50–1.64 Å) and the (H)O–B–O(H) angles were tetrahedral (109.5°) or larger while the O–B–O angles to O atoms of the L^{-2} group were significantly smaller than tetrahedral. As will be seen below, our calculations confirm their results.

It is also interesting that boronic acids ($B(OH)_3$ with some of the OH groups replaced by hydrocarbon groups) are now used as specific complexants to identify particular sugars (James et al., 1996) and other polyalcohols. The interaction of boric acid and borates may also be important in stabilizing and reducing the reactivity of certain sugars, such as ribose, in solution (Ricardo et al., 2004). Thus, borate complexation with polyalcohols or polyacids plays several different roles within solution chemistry and geochemistry.

It should be noted that an alternative to our quantum chemical approach would be to use methods that were still atomistic but that used classical molecular mechanics or molecular dynamics. Parameters needed for the MM or MD simulations could be obtained partly from quantum mechanical calculations. Such methods may well be better for addressing questions in which non-local, e.g. long range electrostatic or conformational effects are important and advances have been made in this area. Such methods have been used to model both the structure of humic acid (Sein et al., 1999; Diallo et al., 2003) and its interaction with pollutants such as phthalates (Schulten et al., 2001).

2. Computational methods

For the calculation of the gas-phase free energies we use the CBS-QB3 method, a "composite" method which determines equilibrium geometries essentially at the 6-311G(d,p) B3LYP (Becke, 1993) level (but with a slightly modified basis set often called CBSB7) and uses a single point CCSD(T) calculation (Scuseria and Schaefer, 1989) with a 6-31+G(d,p) basis set at the 6-311G(d,p) B3LYP geometry (Montgomery et al., 1999) to evaluate electron correlation effects. The vibrational spectrum is also calculated at the (harmonic) CBSB7 B3LYP level and the absence of imaginary frequencies confirms that we are at a

local minimum. As discussed by Montgomery et al. (1999), CBS-QB3 is a highly accurate approach for the determination of reaction free energies, typically producing errors around 1 kcal/mol. Unfortunately, the computer time required for the CCSD(T) step in our implementation scales as about the seventh power of the number of orbitals and the disk space required scales as about the fourth power of the number of orbitals, so the method becomes very demanding computationally for the larger $B(OH)_2L^-$ species.

To evaluate the hydration free energies we use the conductor polarizable continuum method (CPCM; Truong and Stefanovitch, 1995), a version of the polarizable continuum method (PCM; Tomasi, 2004). There are many different versions of the PCM, but none which give hydration free energies for singly-charged anions with average absolute errors of less than about 1–2 kcal/mol, vs. experiment. Thus, although the hydration term in the reaction free energy is often smaller in magnitude than the gas-phase term, the absolute error in its calculation is probably larger.

We have also calculated ^{11}B NMR shieldings and shifts for all of the species considered, to establish additional criteria for their identification, using the GIAO version of coupled Hartree–Fock perturbation theory (Wolinski et al., 1990). We have utilized 6-311+G(2d,p) basis sets and the HF method. Unfortunately these complexes are too large for large basis set MP2 calculations, so we cannot employ the scaling procedure of Chesnut (1995) to estimate the infinite order MP result. We have calculated the ^{11}B NMR shielding for the gas-phase reference compound $(C_2H_5)_2OBF_3$ using the same method and basis set and have calculated shifts compared to this reference. In our evaluation of the nuclear quadrupole coupling tensor for the ^{11}B nucleus we used the nuclear quadrupole moment value recommended by Pyykko (1992) to convert electric field gradients to values of nuclear quadrupole coupling, C_Q.

To evaluate the isotopic fractionations for isotopomers with different central atom (i.e. B) isotopes we simply evaluate the vibrational, rotational and translational contributions to the free energy, which includes the zero-point vibrational energy, but is not necessarily dominated by it. The present work on isotopic fractionation must be considered somewhat preliminary, since we have not systematically studied the dependence of the calculated fractionations on basis set or method and have not considered the effect of the aqueous medium. We have also not used any scaling factors to adjust the calculated and experimental frequencies (Scott and Radom, 1996). Previous studies of B isotope fractionation for the $B(OH)_3$, $B(OH)_4^-$ pair which studied the effects of hydration (Yamahira and Oi, 2004; Liu and Tossell, 2005) found it to be on the order of 1–2 ‰. In any case, any quantitative comparison of solution and adsorbate complexes is dependent upon our assumption that adsorption has little effect upon the properties of the complexes.

All calculations were done using GAUSSIAN03 (Frisch et al., 2003) and the structures of the complexes were displayed using GaussView (Frisch et al., 2003). All the calculations were performed on PowerMac G5 Dual or Quad desktop computers under Mac OS X. Since the version of GAUSSIAN we used is designed for a 32-bit computer architecture we could address only 16 GB of disk, which prevented us from doing CBS-QB3 calculations for the $B(OH)_2L^-$ species with more than 9 non-H atoms. Thus, we were limited by the program architecture rather than by main memory or disk size or CPU speed.

3. Results and discussion

3.1. Structural and spectral properties of $B(OH)_2L^-$ complexes

Calculated properties for $B(OH)_3$, $B(OH)_4^-$ and for various complexes of the type $B(OH)_2L^-$ are given in Table 1. We list calculated ^{11}B NMR shieldings and shifts (σ^B and δ^B), free energy differences of ^{11}B and ^{10}B isotopomers ($G_{11}-G_{10}$) and isotopic fractionations δ 11B compared to $B(OH)_3$, along with B–O bond distances and the angles O–B–O spanned by the O atoms of L (for the ring complexes). Unfortunately the nomenclature is necessarily a bit confusing, since "δ" is traditionally used in both NMR spectroscopy and in stable isotope fractionation studies. In this study, we will use δ^B to indicate NMR shifts and δ 11B to indicate isotopic fractionations.

The calculated values for $B(OH)_3$ and $B(OH)_4^-$ were previously reported and discussed (Tossell, 2005b). Pictures of the $B(OH)_2L^-$ complexes are shown in Fig. 1. The only 6-ring diphenol structure we were able to find was that derived from a naphthalene skeleton. The single ring 1,3 diphenol species (resorcinol) did not form a bidentate complex with $B(OH)_3$, due apparently to angle strain, since the angle between the C–O$^-$ bonds and their adjacent C–C bonds must be seriously deformed to bring the two O atoms close enough to form a bidentate connection to the B. Note that for $B(OH)_2CO_3^-$ there are two different isomeric forms, one with four-coordinate B (BIV) in a closed 4-ring and one with three-coordinate B (BIII) in an open corner-sharing structure. These differ in free energy in solution by only 6 kcal/mol.

Calculated energetics for reactions to form the $B(OH)_2L^-$ species are presented in Table 2. Unfortunately, our methods do not give the same accuracies and reliablities for all the different properties considered. We would in general expect our CBSB7 B3LYP methods to give very accurate geometries and vibrational frequencies for the complexes in the gas phase. The 6-311+G(2d,p) GIAO HF methods should also give very accurate NMR shifts vs. $B(OH)_4^-$, although the absolute shieldings may be in error. Neglect of solvent effects would probably produce larger errors for the vibrational frequencies than for the geometries and NMR shifts. The hardest quantities to calculate are by far the reaction free energies. This is basically

Table 1
Calculated ^{11}B NMR shieldings and shifts (vs. $(C_2H_5)_2OBF_3$ at 0 ppm), free energy differences (kcal/mol) of ^{11}B and ^{10}B isotopomers, δ 11B fractionations vs. $B(OH)_3$ and B–O distances and O–B–O angle within ring (where present)

Molecule	σ^B (ppm)	δ^B (ppm)	$G_{11} - G_{10}$	δ 11B (‰) vs. $B(OH)_3$	R(B–O) Å (<O–B–O°)
$(C_2H_5)_2OBF_3$	115.3	0 reference			
$B(OH)_3$	95.6	+19.7	-0.2102	0	3 × 1.369
$B(OH)_4^-$	114.2	+1.1	-0.1914	-31	4 × 1.486
$B(OH)_2C_2O_4^-$ 5-ring dicarboxylic (oxalic acid)	111.7	+3.6	-0.1895	-34	1.425, 1.436 1.527, 1.554 (100.6)
$B(OH)_2C_3O_4H_2^{-1}$ 6-ring dicarboxylic (malonic acid)	113.8	+1.5	-0.1901	-33	2 × 1.446 2 × 1.513 (112.2)
$B(OH)_2C_4O_4H_4^-$ 7-ring dicarboxylic (succinic acid)	115.0	+0.3	-0.1857	-41	2 × 1.446 2 × 1.520 (116.1)
$B(OH)_2C_2H_4O_2^-$ 5-ring diol (ethylene glycol)	111.0	+4.3	-0.1895	-34	1.456, 1.468 1.504, 1.523 (102.7)
$B(OH)_2C_6H_4O_2^-$ 5-ring phenolic (catechol)	108.8	+6.5	-0.1884	-36	2 × 1.450 2 × 1.532 (102.6)
$B(OH)_2C_{10}H_6O_2^{-1}$ 6-ring phenolic (1,8 dihydroxy-naphthalene)	114.9	+0.4	-0.1895	-34	1.442, 1.457 1.508, 1.509 (110.1)
$B(OH)_2CH_3CO_2$ corner-sharing carboxylic (acetic acid)	95.3	+20.0	-0.2052	-8	2 × 1.360, 1.404
$B(OH)_2C_2O_3H_2^-$ 5-ring glycolate (glycolic acid)	109.9	+5.4	-0.1901	-33	1.443,1.447, 1.498,1.559 (101.3)
$B(OH)_2CO_3^-$ 4-ring carbonate (H_2CO_3)	113.5	+1.8	-0.1895	-34	1.423, 1.437 1.538, 1.568 (84.7)
$B(OH)_2CO_3^-$ corner-sharing carbonate (H_2CO_3)	96.5	+18.8	-0.2033	-12	1.319, 1.406, 1.415

The name of the parent neutral ligand is given in parentheses.

because the gas-phase and hydration contributions to the aqueous solution free energy are often of opposite sign and comparable size and the accuracy of the gas-phase result is higher than that of the hydration free energies calculated using the CPCM method.

The $B(OH)_2L^-$ complexes fall into two groups, those which have (roughly) trigonal three-coordinate B (BIII) with corner-sharing O structures and those which have (roughly) tetrahedral four-coordinate B (BIV), with closed ring structures. The BIV species have much less positive B NMR shifts and much more negative δ 11B while the BIII species have large positive B NMR shifts and small δ 11B. Despite repeated efforts we were unable to find a BIII isomer of $B(OH)_2C_2O_4^-$ or a BIV isomer of $B(OH)_2CH_3CO_2$.

There is little variation of ^{11}B NMR shift for the different three-coordinate species $B(OH)_3$, $B(OH)_2CH_3CO_2^-$ and the corner-sharing isomer of $B(OH)_2CO_3^-$, although the δ 11B does show significant variation. For the four-coordinate species $B(OH)_4^-$, $B(OH)_2C_2O_4^-$, $B(OH)_2C_2H_4O_2^-$ $B(OH)_2C_3 O_4H_2^-$, $B(OH)_2C_6H_4O_2^-$, $B(OH)_2C_{10}H_6O_2^-$, $B(OH)_2C_2O_3H_2^-$ and the four-coordinate ring version of $B(OH)_2CO_3^-$ there is about a 6 ppm range in NMR shift and the δ 11B values show a range of about 5‰. The 4-ring $B(OH)_2CO_3^-$ complex has a shift of +1.8 ppm, very similar to that of $B(OH)_4^-$. For the 4-ring $B(OH)_2CO_3^-$ complex we have also evaluated the NMR shielding at the correlated B3LYP and MP2 levels (see Gauss and Stanton, 2002 for a discussion of these methods) and find that it differs in shielding from $B(OH)_4^-$ by less than 1 ppm no matter which computational level is used.

Trends in NMR shifts are consistent with those observed experimentally (van Duin et al., 1984); e.g. the 5-ring dicarboxylic oxalate complex with a shift of +3.6 is deshielded compared to the 6-ring malonate complex with a shift of +1.5 ppm. The 7-ring succinate complex is even more strongly shielded with a shift of only 0.3 ppm. Similarly, the 5-ring diphenolic complex with a shift of +6.5 is strongly deshielded compared to the 6-ring diphenolic complex of dihydroxynaphthalene, with a shift of only +0.4 ppm. These results are consistent with the general principle that (all other things being equal) network-forming elements in small oxidic rings are deshielded compared to those in larger rings. Such effects are often seen as well in silicates (Kemmitt and Milestone, 1995). All the four-coordinate complexes of $B(OH)_2L^-$ type show δ 11B values slightly more negative than $B(OH)_4^-$. However, the differences in either NMR shift or isotopic fractionation between the four-coordinate $B(OH)_2L^-$ complexes and $B(OH)_4^-$ itself are fairly small.

There is considerable experimental ^{11}B NMR data on the stable catechol and oxalic acid complexes of $B(OH)_3$. Unfortunately, the literature must be read with care since many of these studies were done near the dawn of ^{11}B NMR spectroscopy, when there was little agreement on the primary or secondary chemical shift refer-
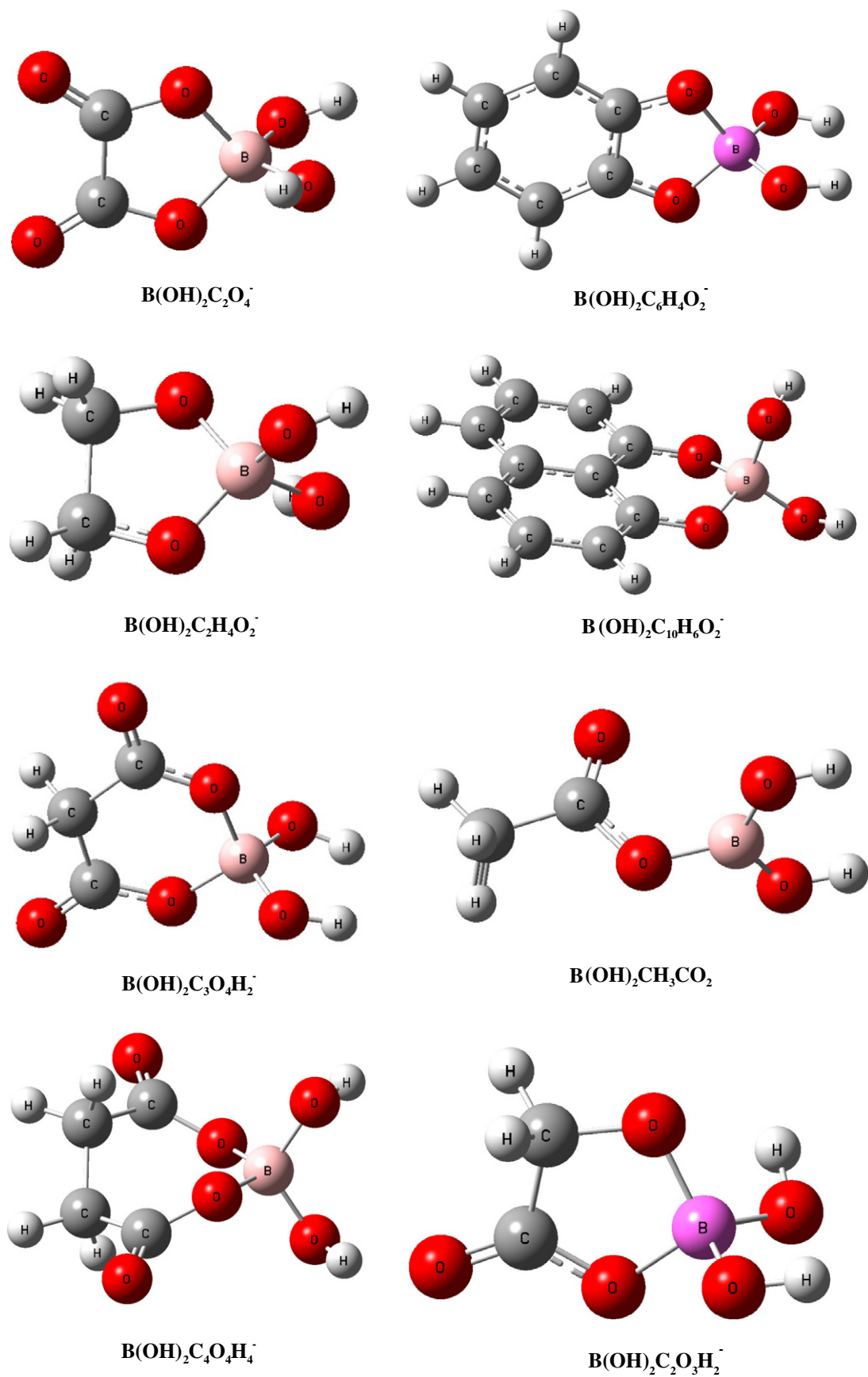
$B(OH)_2C_2O_4^-$

$B(OH)_2C_6H_4O_2^-$

$B(OH)_2C_2H_4O_2^-$

$B(OH)_2C_{10}H_6O_2^-$

$B(OH)_2C_3O_4H_2^-$

$B(OH)_2CH_3CO_2$

$B(OH)_2C_4O_4H_4^-$

$B(OH)_2C_2O_3H_2^-$

Fig. 1. Calculated equilibrium geometries for $B(OH)_2L^-$ complexes.

B(OH)$_2$CO$_3^-$
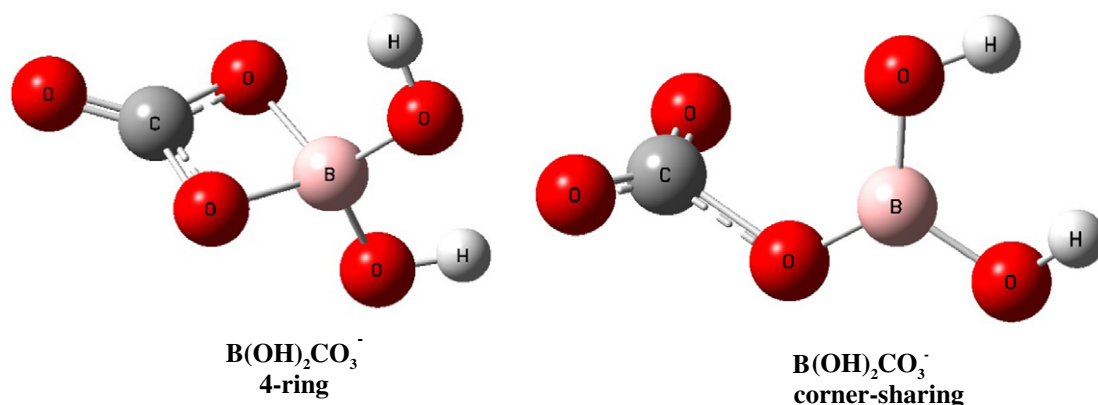**4-ring**

B(OH)$_2$CO$_3^-$
corner-sharing

Fig. 1 (*continued*)

Table 2
Calculated gas-phase, hydration and total free energies (in kcal/mol) from CBSB7 B3LYP and CBS-QB3 calculations, along with best calculated value of log K, for reactions of type: B(OH)$_3$ + HL$^-$ ⇒ B(OH)$_2$L$^-$ + H$_2$O

HL$^-$/parent ligand	ΔG CBSB7 B3LYP	ΔG CBS QB3	ΔG CPCM	$\Delta G_{aq}\Delta G$ CBSB7 B3LYP + ΔG CPCM	$\Delta G_{aq}\,\Delta G$ CBS-QB3 + ΔG CPCM	Scaled ΔG_{aq} CBSB7 B3LYP + ΔG CPCM	Log K at 25 °C
C$_2$O$_4$H$^-$ oxalic acid	−14.1	−20.7	+14.9	+0.8	−5.8	−5.5	+ 4.2
C$_2$H$_5$O$_4^-$ ethylene glycol	−26.0	−33.4	+18.1	−7.9	−15.3	−15.3	+ 11.2
C$_3$O$_4$H$_3^-$ malonic acid	−8.9	n.a.	+14.0	+5.1	n.a.	−0.6	≈ + 0.4
C$_4$O$_4$H$_5^-$ succinic acid	+10.3	n.a.	+2.6	+12.9	n.a.	+9.5	≈ −6.9
C$_6$H$_5$O$_2^-$ catechol	−4.2	n.a.	+1.8	−2.4	n.a.	−7.6	≈ + 5.6
C$_{10}$H$_7$O$_2^-$ 1,8 hydroxy naphthalene	+3.2	n.a.	−2.6	−0.6	n.a.	−3.9	≈ + 2.9
CH$_3$CO$_2$H acetic acid	+16.1	+11.2	−2.8	+13.3	+8.4	+10.2	−6.2
C$_2$O$_3$H$_3^-$ glycolic acid	−3.1	−10.1	+8.3	+5.2	−1.8	+0.4	+1.3
HCO$_3^-$ 4-ring carbonic acid	−2.0	−8.2	+14.1	+12.1	+5.9	+7.1	−4.3
HCO$_3^-$ corner-sharing carbonic acid	+8.2	+7.4	+4.5	+12.7	+11.9	+8.8	−8.7

n.a., not available due to computational limitations.

ences to be used, so that some shifts are reported compared to B(OH)$_3$(aq) while others are reported compared to external (C$_2$H$_5$)$_2$OBF$_3$ or internal B(OH)$_4^-$ (the two of which differ in shift by only about 1 ppm, McKenzie and Smith, 2002). All our calculated shifts are referenced to (C$_2$H$_5$)$_2$OBF$_3$.

In our earlier study (Tossell, 2005b) we established that our methods give an NMR shift difference between B(OH)$_3$ and B(OH)$_4^-$ that was in good agreement with experimental data, with calculated differences at the Hartree–Fock level of 18.6 ppm and the infinite order MPn level of 16.8 ppm, and experimental differences in solution of about 17 ppm (Smith and Wiersma, 1972) and in solid silicates of about 15–16 ppm (Turner et al., 1986). We calculate shifts of +1.1 and +19.7 for B(OH)$_4^-$ and B(OH)$_3$, respectively. The shift of aqueous B(OH)$_2$C$_6$H$_4$O$_2^-$ with respect to B(OH)$_4^-$ has been reported as 5.6 ppm (Yoshino et al., 1979), 6.1 ppm (Pasdeloup and Brisson, 1981) and 5.0–5.2 ppm (Mohr et al., 1990). These convert to shifts with respect to (C$_2$H$_5$)$_2$OBF$_3$ of 6.7, 7.2 and 6.3 ppm, respectively, compared to our calculated value of +6.5 ppm. For B(OH)$_2$C$_6$H$_4$O$_2^-$ we have also performed NMR calculations at the correlated B3LYP level, obtaining a shift of about 7.3 ppm, so that correlation effects on the shifts seem

to be fairly small. The ethylene glycol complex B(OH)$_2$C$_2$H$_2$O$_2^-$ is reported by Van Duin et al. (1984) to be deshielded by about 0.6 ppm with respect to the oxalic acid complex, which is consistent with our calculated shielding difference of 0.7 ppm, given in Table 1. Overall, our calculated shieldings seem to reproduce the experimental shift trends quite well. Based on the relative shifts given in Table 2 of Schmitt-Kopplin et al. (1998) the shift of the oxalic acid complex B(OH)$_2$C$_2$O$_4^-$ relative to the catchol complex is −3.5 ppm, so its shift with respect to B(OH)$_4^-$ is +2.6 ppm. Our value calculated at the 6-311+G(2d,p) HF level is +2.5 ppm.

Lemarchand et al. (2005) observed ^{11}B NMR peaks at about 1.2–1.6 and 5.6 ppm (referenced to (C$_2$H$_5$)$_2$OBF$_3$) for boric acid absorbed on humic acid, at both pH 6 and 9. They assigned the 1.2–1.6 ppm peak to a 6-ring 1,3 diol complex, based on the assignments in Schmitt-Kopplin et al. (1998) for aqueous complexes. Their experimental value of 1.2–1.6 for one of the humic acid complexes is close to our calculated value of +1.5 ppm for the shift of the 6-ring dicarboxylic acid species, derived from malonic acid. They assigned the 5.6 ppm peak to a 5-ring 1,2 diol complex, probably phenolic in structure, again based on the aqueous solution complex study of Schmitt-Kopplin

et al. (1998). It is clear from the data in Table 1 that the only species giving ^{11}B shifts in the range of 5–6 ppm are 5-ring BIV species, i.e. the 5-ring glycolic acid species (an α-hydroxy carboxylic acid) at 5.4 ppm and the 5-ring diphenolic species at +6.5 ppm. Glycolic acid has a 1st pK_a of about 3.8, so that it would be deprotonated at pH 6 and could readily react with $B(OH)_3$, with a calculated $\log K$ for complex formation of +1.3 (Table 2). This species was not considered by Lemarchand et al. (2005) or Schmitt-Kopplin et al. (1998). Catechol (the 1,2 diphenol) has a 1st pK_a of about 9.2 so would be partially deprotonated at pH 9. Its calculated $\log K$ for complex formation is +5.3. Thus, our interpretation based on the present data would be that the ^{11}B NMR peak observed around 1.2–1.6 ppm should be attributed to a 6-ring dicarboxylic acid complex, like that of malonic acid, and the peak around 5.6 ppm could arise from a 5-ring glycolic acid-like complex or from complexation with a 1,2 diphenol, like catechol.

3.2. Comparison with the models of Lemarchand et al. (2005) for δ 11B

In Lemarchand et al. (2005) many of the δ 11B values obtained by their modeling procedure for the boric acid-humic acid surface complex models fell within the range of the mid −20's while a few were in the range of −40's. They contrasted these with an assumed value of about −19‰ for $B(OH)_4^-$, based on the equilibrium isotopic fractionation constant of 1.0194 given by Kakihana et al. (1977). However, this value has now been superseded by the direct experimental determination of the equilibrium constant for isotopic fractionation between aqueous $B(OH)_3$ and $B(OH)_4^-$ by Byrne et al. (2006) and Klochko et al. (2006). These values, obtained directly by measuring the pK_a difference of >99% isotopically enriched $^{10}B(OH)_3$ and $^{11}B(OH)_3$, give K's for the isotopic exchange reaction around 1.028 for ionic strength of 0.63 and 1.030 for pure water, corresponding to δ 11B values of about −28‰ to −30‰ for $B(OH)_4^-$. Quantum mechanical calculations by Oi (2000) and Liu and Tossell (2005) give similar values. In fact, experimental data from the Kakihana group (Oi et al., 1991) and from Sanyal et al. (2000) have also indicated that the Kakihana et al. (1977) equilibrium constant value was too small. Sanchez-Valle et al. (2005) have obtained a K value even smaller using a set of experimental vibrational frequencies obtained from a variety of sources, but Zeebe (2005) has pointed out the dangers involved in such selection of vibrational data from the literature.

The calculated δ 11B values for $B(OH)_4^-$ and all the BIV type complexes considered are in the range from −31‰ to −41‰, as shown in Table 1. Note that these δ 11B values were obtained using unscaled vibrational frequencies and the 6-311(d,p) basis and B3LYP method. Using vibrational frequencies with scaling factors typically used at this quantum mechanical level to obtain the best fit to experimental frequencies (a factor around 0.96, Scott

and Radom, 1996) gives a δ 11B value of −30 rather than −31‰ for $B(OH)_4^-$. The values in Table 1 also do not correct for the effect of the aqueous environment on $B(OH)_3$ and $B(OH)_4^-$, which could change δ 11B by 1‰ or 2 ‰ (Yamahira and Oi, 2004; Liu and Tossell, 2005). It seems unreasonable to systematically try to correct for this effect at present since we have no good way to make the corresponding correction for the $B(OH)_2L^-$ surface complexes. We have carried out calculations on the complexes $B(OH)_3$, $B(OH)_4^-$ and 4-ring $B(OH)_2CO_3^-$ within a PCM appropriate to water and have found that their δ 11B values are changed only from 0, −31 and −34 to 0, −28‰ and −33‰ (with $B(OH)_3$ as the reference zero). Thus, hydration efforts appear to cause fairly small changes in the isotopic fractionations of the different complexes.

We can reliably say that the calculated δ 11B values for all the BIV type $B(OH)_2L^-$ complexes are slightly more negative than that for free $B(OH)_4^-$. The most isotopically light complexes we have found are $B(OH)_2C_6H_4O_2^-$, the catecholate complex with δ 11B = −36‰ and $B(OH)_2C_4O_4H_4^{-1}$, the succinate complex with δ 11B = −41‰. In the next section we establish that the log formation constants are positive for the catecholate complex but negative for the succinate. The catecholate complex would be expected to form only at fairly high pH values ($pK_{a1} \approx 9.2$ for catechol), where the catechol is deprotonated to form HL^-. In fact, the complexes fit by Lemarchand et al. (2005) to their data show the most negative δ 11B values for complexes contributing to adsorption mostly in the high pH region (e.g. they report a complex with fitted $pK_a = 9.1$ and fitted δ 11B = −46‰).

In the structures of the four-coordinate $B(OH)_2L^-$ complexes we invariably find that bond distances to the O atoms of the ligand L are larger than those to the –OH groups, e.g. values of 1.527 and 1.554 Å to the two O atoms of the oxalate ligand and 1.425 and 1.436 Å to the two OH groups in $B(OH)_2C_2O_4^-$. The O–B–O angle spanning the two O atoms of L and the B is also often smaller than the tetrahedral angle, having a value of 100.6 in $B(OH)_2C_2O_4^-$. This is suggestive of more distortion and less stability in the $B(OH)_2L^-$ complexes compared to $B(OH)_4^-$. However, from the data in Table 1 there is no obvious relationship between these measures of distortion in the BIV complexes and the magnitudes of their isotopic fractionations, although larger distortions of the <O–B–O from the tetrahedral value do seem to be correlated with decreased NMR shielding or more positive NMR shift values, e.g. in comparing $B(OH)_2C_6H_4O_2^-$ with a shift of +5.6 and a <O–B–O of 102.6 with $B(OH)_2C_{10}H_6O_2^-$, with a shift of only +0.9 and a <O–B–O of 110.1°.

It is also clear from the calculated equilibrium structures that a certain magnitude of separation between the O atoms on the ligand is necessary for a four-coordinate complex to form. If these two O atoms are bonded to the same C the necessary magnitude of separation is very difficult to obtain without severely lengthening and destabilizing the bonds to the C. While it is difficult to be sure that we have identified

the global minimum on the potential energy surface for these complexes (we know from the absence of imaginary frequencies that we are at least at local minima), we were unable to find a BIV complex for $B(OH)_2CH_3CO_2^-$ or BIII complexes for any of the dicarboxylate or diphenolate species. For $B(OH)_2CO_3^-$, however, we readily found both open corner-sharing three-coordinate species and closed 4-ring four-coordinate species. We also found several species closely related to the two shown for this molecule in Fig. 1 but corresponding to slightly different rotations of the OH group about the single bond between B and O(H), but which did not differ significantly from those shown in Fig. 1 in NMR shielding or isotopic fractionation properties. For the 4-ring isomer of $B(OH)_2CO_3^-$ the C–O distance for the O atoms participating in the 4-ring was 1.344 Å, but even with this long C–O distance the <O–B–O was only 84.7, much less than the tetrahedral value. Thus the 4-ring BIV isomer was still significantly strained. By contrast, in $B(OH)_2C_2O_4^-$ the C–O distances within the 5-ring were only 1.314 Å, but the <O–B–O within the ring was 100.6, much closer to tetrahedral. This is a result of having a two C atom 'spacer' between the O atoms in $B(OH)_2C_2O_4^-$ rather than the single C atom in $B(OH)_2CO_3^-$.

In the crystal structure of adrenalon borate hydrate (Mohr et al., 1990), which has a $B(OH)_2C_6H_4O_2^-$ framework, observed B–O bond distances are 1.44 and 1.46 Å to the OH groups and 1.53 and 1.54 Å to the O atoms of the catecholate group, which compare well with our calculated values (Table 1) of 1.450 and 1.532 Å. Mohr et al. (1990) also present the Raman spectrum of this compound in solution between 500 and 1600 cm^{-1}, finding only four modes which they identify as medium or strong at 748, 823, 1010 and 1367 cm^{-1}, with another weak mode at 540 cm^{-1}, while we find the five calculated modes with the highest Raman intensity at 547, 733, 834, 1025 and 1406 cm^{-1}. However, as is often the case for strong Raman modes, these normal modes show rather symmetric stretching motions (of either the whole molecule or the benzene ring) and their calculated frequencies are almost the same for the ^{11}B and ^{10}B isotopomers. It would be more interesting from the point of view of B isotopic fractionation to study the IR spectra, particularly in the region from about 1000–1200 cm^{-1}, where we calculate intense IR modes at 1073, 1124 and 1166 cm^{-1} for the ^{11}B isotopomer and 1089, 1149 and 1192 cm$_{-1}$ for the ^{10}B isotopomer. All three of these modes involve asymmetric stretching of the BIV group. The details of the calculated vibrational normal modes and frequencies and Cartesian coordinates of the optimized geometries are available for all the $B(OH)_2L^-$ complexes in the Electronic Annex EA-1.

3.3. Energetics for $B(OH)_2L^-$ formation

In Table 2 we present energetic quantities calculated for the formation reactions of complexes of the general type $B(OH)_2L^-$:

$$B(OH)_3 + HL^- \Rightarrow B(OH)_2L^- + H_2O \qquad (1)$$
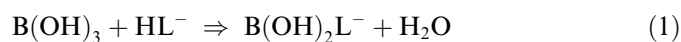
This reaction is in fact very much like the Lewis mechanism for the acidic behavior of $B(OH)_3$:

$$B(OH)_3 + H_2O \Rightarrow B(OH)_4^- + H^+ \qquad (2)$$
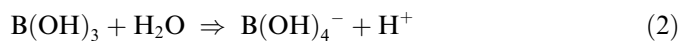
which we previously studied (Tossell, 2005b). It would be desirable to treat all the $B(OH)_2L^-$ complexes at the same CBS-QB3 level used in Tossell (2005b), but this is not feasible computationally for the species with more than 9 non-H atoms. Therefore, for the larger complexes we have only CBSB7 B3LYP free energies (obtained from the CBSB7 B3LYP internal energies and VRT gas phase free energy contributions). For each of the reactions considered we present in Table 2 the CBSB7 B3LYP ΔG values, the CBS-QB3 ΔG values (if available), the reaction free energy of hydration obtained using the CPCM approach, ΔG_{CPCM}, and the sums $\Delta G_{CBSB7\text{-}B3LYP} + \Delta G_{CPCM}$ and $\Delta G_{CBS\text{-}QB3} + \Delta G_{CPCM}$ (for the species with nine or fewer non-H atoms). The first point to note is that the CBSB7 B3LYP and CBS-QB3 free energies consistently differ by around 5 kcal/mol, with the CBS-QB3 values more negative. The internal energy of binding of the complex in the gas-phase becomes more negative by around 5 kcal/mol when correlation and basis-set expansion effects are described by the highly accurate CBS-QB3 approach, rather than the much less accurate CBSB7 B3LYP method. We find that the gas-phase CBSB7 B3LYP and CBS-QB3 free energies are very strongly correlated. Linear regression for the five compounds in Table 2 for which we have free energies at both computational levels gives an equation (energies in kcal/mol):

$$\Delta G_{CBS\text{-}QB3} = 1.105 \Delta G_{CBSB7\text{-}B3LYP} - 4.8 \qquad (3)$$

with a correlation coefficient of 0.99. We call the values obtained from this equation "scaled CBSB7 B3LYP values" and present them in the second to last column in Table 2. We have also evaluated $\log K$ values at 25 °C using the CBS-QB3 values where available and the scaled CBSB7 B3LYP values otherwise. Those $\log K$ values obtained from the scaled CBSB7 B3LYP free energies are identified by approximation symbols before the $\log K$ value in the last column of Table 2. Note also that most of the ΔG_{CPCM} values given in Table 2 are positive, basically since the anion on the product side, $B(OH)_2L^-$, is larger than that on the reactant side, HL^-, and thus its hydration free energy is less negative. This is true except for very large HL^-, such as $C_{10}H_7O_2^-$, and for the neutral ligand CH_3CO_2H.

Based on the ΔG_{aq} values in Table 2 we would expect that the anion of oxalic acid forms a stronger complex than that of malonic acid, that the catechol complex is stronger than either of the dicarboxyolic acid complexes and that the dihydroxynaphthalene complex is similar in stability to oxalate. In general, the complexes in which B is part of a five-membered ring are more stable than the six-membered ring complexes, in agreement with experimental data for a range of metal complexes (Martell and Hancock, 1996, pp. 73–82) and with specific results for boronic esters (Lorber and Pizer, 1976). For example, the approximate

ΔG_{aq} for the 5-membered ring complex with $C_2HO_4^-$ (oxalate) is more negative that for the 6-membered ring complex with $C_3H_3O_4^-$ (malonate) by 4.9 kcal/mol (Table 2). The two 4-membered ring complexes we have examined, $B(OH)_2CH_3CO_2$ and $B(OH)_2CO_3^-$ are quite unstable. This is consistent with the fact that no experimental data apparently exists for monodentate borate esters or for any complexes formed by reaction between $B(OH)_3$ and monocarboxylic acids, like acetic acid (van Duin et al., 1984; Smith and Martell, 1989). According to our calculations, the acetic acid complex exists only in a monodentate BIII form, which it is quite unstable compared to $B(OH)_3$ and the ligand. Thus, $B(OH)_3$ is not an effective probe for monocarboxylic acid sites in humic acid, discriminating strongly in favor of the dicarboxylic acid sites.

The 5-ring glycolate complex, $B(OH)_2C_2H_4O_2^-$, is calculated to be quite stable, but can only form when the ethylene glycol is deprotonated at high values of pH to produce the glycolate anion ($pK_{a1} \approx 15$ for ethylene glycol). More generally, we should note that the complex formation reaction (1) involves HL^- as a reactant. The first pK_a's for some relevant H_2L species are 1.2, 15.4, 2.8, 9.2 and 4.8 for oxalic acid, ethylene glycol, malonic acid, catechol and acetic acid, respectively. Thus, formation of the necessary HL^- species from neutral ethylene glycol is much harder than its formation from oxalic acid, requiring an additional free energy expenditure of about 19.5 kcal/mol (at 298 K, obtained as $\Delta pK_a \times 1.3644$ kcal/mol). Only under pH conditions in which $C_2H_5O_4^-$ already exists as the main ethylene glycol species can it interact with $B(OH)_3$ to give the $B(OH)_2L^-$ complex.

Obtaining quantitative comparisons of calculated and experimental equilibrium constants for reactions of type (1) is still very difficult. First, obtaining accurate calculated reaction free energies in solution is very difficult, because our methods for assessing hydration contributions are not very accurate. This is true even though we have been careful to select a reaction type which is both isocoulombic (the sums of squares of charges are equal for reactants and products), so as to reduce the free energy of hydration for the reaction and isomolar (same number of moles for reactants and products), to reduce entropic effects. There is also considerable ambiguity in the experimental results. The first point to note is that there are two different prominent complexes near slightly alkaline pH in $B(OH)_3$(aq) solutions, $B(OH)_3$ and $B(OH)_4^-$, and the ligands can also exist in a number of different charge states, from L^{-2}, through HL^- to H_2L. Experimental reactions are not always written with the proper charge state, which may be unknown. Experimental definitions of equilibrium constants also generally leave out the concentration of H_2O, which is essentially fixed at about 55 M in aqueous solution. They should therefore be corrected for this effect before comparison with the calculated values. As best we can determine, the association constant for the specific oxalate complexation reaction

$$B(OH)_3 + C_2HO_4^- \Rightarrow B(OH)_2C_2O_4^- + H_2O \quad (4)$$

with the general form of Reaction (1), which can also be expressed (Van Duin et al., 1984) as:

$$B^0 + L^- \Rightarrow BL^- + H_2O \quad (5)$$

has a K value of 2.9 (Van Duin et al., 1984; Table 3). Lemarchand et al. (2005) report $\log K_{BL^-}$ values of 2.5–2.9, which appear to correspond to a very similar reaction for the more acidic sites on humic acid, which they associate with dicarboxylic acids. After multiplying by 55 to correct for the molarity of H_2O we thus obtain $\log K$ values of 2.2 for the van Duin complex and around 4.4 for the complexes identified by Lemarchand et al. (2005). These would translate into room temperature ΔG values of about -3.0 and -6.0 kcal/mol, respectively, while our calculated ΔG_{aq} for this reaction (Table 2) is -5.8 kcal/mol. It is not clear whether the solution complex studied by van Duin et al. (1984) and the surface complex studied by Lemarchand et al. (2005) are the same, and expecting our calculated value of ΔG_{aq} to be accurate to better than 2–3 kcal/mol would probably be unreasonable. The comparison of calculated and experimental energetics does not appears to work even this well for the complex $B(OH)_2CO_3^-$ studied by McElligott and Byrne (1998). They obtain an average K value of 2.6 (although with a large experimental error), which when multiplied by the molarity of water and converted to a reaction free energy would give $\Delta G = -2.9$ kcal/mol, while we calculate $+5.9$ kcal/mol (Table 2). It is conceivable that we have not identified the most stable rotamer(s) of $B(OH)_2CO_3^-$ in solution or that our value for the hydration free energy of the small anion reactant HCO_3^- is too negative. At present we are confident of our qualitative ordering of reaction free energies for the $B(OH)_2L^-$ species, but not of their quantitative values.

3.4. Correlation of structures and isotopic fractionations

It was noted long ago that the sense of many isotopic fractionations can be understood using the concept that "the heavy isotope goes preferentially to the chemical compound in which the element is bound most strongly" (Bigeleisen, 1965). In general we would anticipate that three short, strong B–O bonds in BIII complexes would

Table 3
Calculated NMR and NQR properties (using ^{11}B nuclear quadrupole moment from Pyykko, 1992) for the corner-sharing BIII and the 4-ring BIV isomers of $B(OH)_2CO_3^-$

Property	BIII isomer	BIV isomer
σ (in ppm) (isotropic value same as in Table 1)	96.5	113.5
$\Delta\sigma$ (in ppm)	28.0	27.5
q_{ii} (in au)	$-0.327, +0.076, +0.251$	$-0.109, +0.002, +0.107$
C_Q (in MHz)	3.15	1.05
η	0.54	1.0

give stronger overall bonding than four long, weak bonds in BIV complexes. We can quantify this concept using the relationship between bond length and bond strength established by Brown's group (e.g. Brown and Altermatt, 1985). We can express the strength of a bond, s_i, as:

$$s_i = \exp[(r_0 - r_i)/B] \qquad (6)$$

where $r_0 = 1.371$ Å for B–O bonds and $B = 0.37$ and we use the CBSB7 B3LYP calculated geometries to obtain the r_i. We then sum all the calculated bond strengths to the B atoms for the complexes in Table 1 and present a scatter plot of these bond strength sums vs. the δ 11B values in Fig. 2. It is apparent that there is some correlation of bond strength sums with δ 11B values but that it is a fairly weak one, with most of the BIV complexes having fractionations more negative than suggested by their bond strength sums. For the BIII species near the top of Fig. 2 the correlation seems considerably better. The problem may be that the Brown approach considers only bond distances, while relative energies for the BIV species may be influenced as much by bond angles. Of course it is also true that the energy variations which occur near minima on the potential energy surface and which are better measured by harmonic force constants are really more important than the overall bond strengths in determining the fractionation. Stretching force constants are correlated with bond lengths (Badger's rule, Cioslowski et al., 2000), and therefore with Brown bond strengths, but only to a moderate extent.

3.5. $B(OH)_2CO_3^-$ as a possible B impurity site in calcite

Although McElligott and Byrne (1998) studied $B(OH)_2CO_3^-$ in solution, it is intriguing to explore the possibility that it might constitute the site of B impurities in calcium carbonates, which have been studied by Sen et al. (1994) using ^{11}B NMR. One surprising result of the Sen et al. ^{11}B NMR study was the identification of a preponderance of BIII in the calcites (with about 20% BIV) but only BIV in the aragonites. The NMR shifts and nuclear quadrupole coupling constant, C_Q, values found were fairly typical for B in three- and four-coordinate oxidic environments, although the nuclear quadrupole asymmetry parameter, η, was larger than normally observed for BIII (0.67 vs. a normal 0.06–0.12). These species have typically been interpreted as monomers such as $BO_2(OH)^{-2}$, substituting at carbonate positions (Hemming and Hanson, 1992; Hemming et al., 1995). Indeed, we have shown (Tossell, 2005b) that the NMR shielding and nuclear quadrupole asymmetry calculated for $BO_2(OH)^{-2}$ (and $BO(OH)_2^-$) are consistent with the ^{11}B NMR of Sen et al. (1994). However, the acid dissociation reaction of $B(OH)_3$ actually produces the species $B(OH)_4^-$ rather than $BO(OH)_2^-$, a species for which the calculated pK_a is higher by around 10 units, corresponding to roughly 14 kcal/mol higher free energy (Tossell, 2005b). The further deprotonated species $BO_2(OH)^{-2}$ must of course be even higher in energy. Also, there is strong evidence that the surface of calcium carbonate minerals in contact with water possesses both HCO_3^- groups and OH^- groups (Stipp, 1999, 2002). Features in the surface IR of acid-treated $CaCO_3$ have also been recently assigned to H_2CO_3 species (Al-Hosney and Grassian, 2004). Thus, there is the possibility that boric acid or borate groups approaching the calcium carbonate surface could interact with HCO_3^-, as in reaction (1). It is therefore worthwhile to examine the NMR and nuclear quadrupole coupling properties of the two different
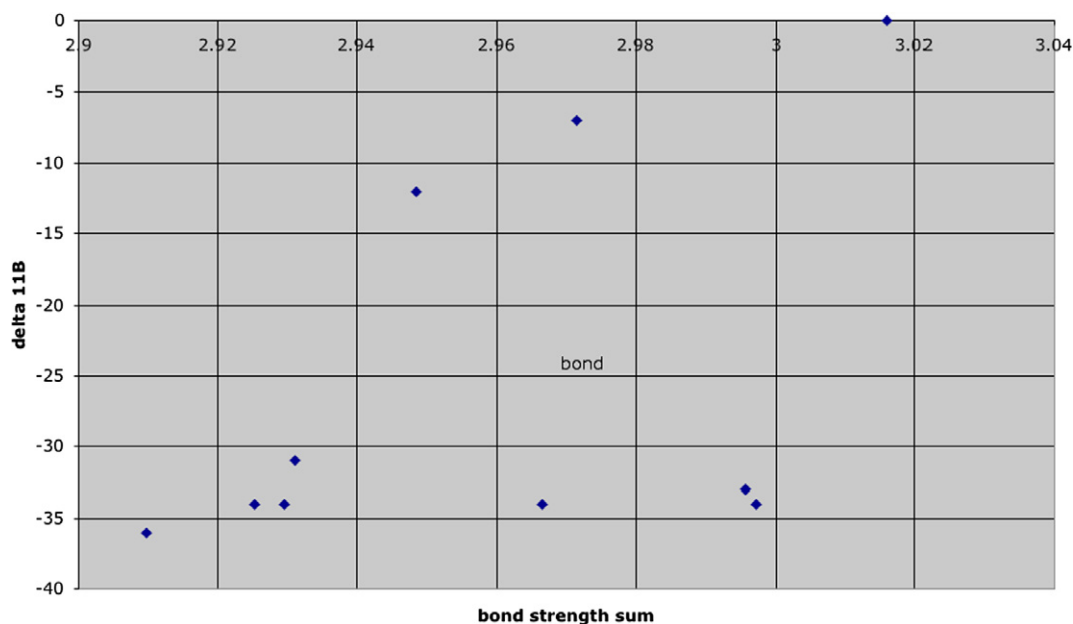

Fig. 2. Scatter plot of δ 11B (‰) vs. bond strength sum for $B(OH)_3$, $B(OH)_4^-$ and $B(OH)_2L^-$, with bond strength sums calculated from bond distances in Table 1.

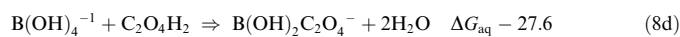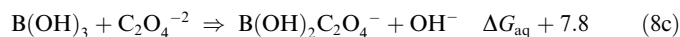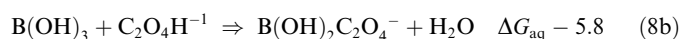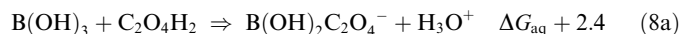isomers of $B(OH)_2CO_3^-$ more closely, as shown in Table 3. We see that the corner-sharing carbonate BIII isomer has a calculated NMR shielding of 96.5 ppm, almost the same value as that for $B(OH)_3$, a calculated C_Q value of 3.15 MHz and a calculated η value of about 0.54. These values are all consistent with those reported for the "BO3" species in Sen et al. (1994). The 4-ring carbonate BIV species has a calculated NMR shielding of 113.5 ppm, and C_Q and η values of 1.05 MHz and about 1, respectively. The substantial values of C_Q and η are of course consistent with a distorted, rather than a highly symmetrical, BIV site. The experimental data of Sen et al. (1994) apparently show a more symmetrical site. The fit of properties for the two different $B(OH)_2CO_3^-$ species with experiment is therefore suggestive, but probably not completely convincing. But it has been noted by Sen et al., that obtaining accurate NMR and NQR parameters for samples with such low B concentrations is difficult. The presence of two different $B(OH)_2CO_3^-$ isomers, with BIII or BIV but with fairly similar free energies, is certainly interesting. A possible technique for identifying such a species would be a surface specific vibrational technique, such as reflection IR. Su and Suarez (1995) studied the absorption of $B(OH)_3$ on a number of different minerals, including calcite, but the adsorption on calcite was too small to show any changes in IR spectra. Of course, adsorption on an already formed surface and incorporation as an impurity in a growing crystal are not necessary the same thing.

In the study of McElligott and Byrne (1998) the pH values used were near the 1st pK_a of $B(OH)_3$ and above that of H_2CO_3, so that $B(OH)_3$ and HCO_3^- would have been prominent solution species and their reaction to form $B(OH)_2CO_3^-$ would probably be the most favorable complexation reaction possible. We have also calculated the free energy for reaction between $B(OH)_4^-$ and HCO_3^-:

$$B(OH)_4^- + HCO_3^- \Rightarrow B(OH)_2CO_3^- + H_2O + OH^- \quad (7)$$

in the same way as for reaction type (1). The gas-phase CBS-QB3 free energy change for this reaction (for the most stable 4-ring isomer of $B(OH)_2CO_3^-$) is +35.5 kcal/mol while the hydration free energy change is −28.4 kcal/mol (mainly because of the highly negative hydration free energy for OH^-), for an overall ΔG_{aq} of +7.1 kcal/mol. This free energy change is only slightly more positive (by 1.2 kcal/mol) than for the reaction involving neutral $B(OH)_3$. More realistically, both reactions have free energies close enough to zero that slight complications in the reaction scheme, related to the presence or absence of solvent and/or counterions, could shift their balance of thermodynamic favorabilities.

More generally we can systematically compare the calculated energetics for similar reactions involving different charge states of boric acid/borate and the ligand. Using the same method used to generate the entries in Table 2 we arrive at the following ΔG_{aq} values for formation of the $B(OH)_2C_2O_4^-$ complex by different reaction paths

$$B(OH)_3 + C_2O_4H_2 \Rightarrow B(OH)_2C_2O_4^- + H_3O^+ \quad \Delta G_{aq} + 2.4 \quad (8a)$$

$$B(OH)_3 + C_2O_4H^{-1} \Rightarrow B(OH)_2C_2O_4^- + H_2O \quad \Delta G_{aq} - 5.8 \quad (8b)$$

$$B(OH)_3 + C_2O_4^{-2} \Rightarrow B(OH)_2C_2O_4^- + OH^- \quad \Delta G_{aq} + 7.8 \quad (8c)$$

$$B(OH)_4^{-1} + C_2O_4H_2 \Rightarrow B(OH)_2C_2O_4^- + 2H_2O \quad \Delta G_{aq} - 27.6 \quad (8d)$$

$$B(OH)_4^{-1} + C_2O_4H^{-1} \Rightarrow B(OH)_2C_2O_4^- + H_2O + OH^- \quad \Delta G_{aq} - 7.0 \quad (8e)$$

$$B(OH)_4^{-1} + C_2O_4^{-2} \Rightarrow B(OH)_2C_2O_4^- + 2OH^- \quad \Delta G_{aq} + 6.5 \quad (8f)$$
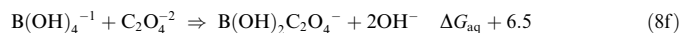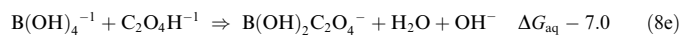
It is clear that there is a trend in this data—when the sum of the charges on the B-containing and ligand reactants is the same as that on the product complex (−1 for the case of $B(OH)_2C_2O_4^-$) the reaction free energy is most favorable. This result is consistent with the "charge rule" developed by Van Duin et al. (1984) to explain their experimental data on formation constants, which states that "esters of boric acid and borate in aqueous medium show the highest stability at that pH where the sum of the charges of the free esterifying species is equal to the charge of the ester". Since the protonation state of both boric acid/borate and the ligand species vary with pH this allows us to predict the most favorable pH for formation of a particular product. Note however that the reaction energetics of $B(OH)_3$ and $B(OH)_4^-$ with $C_2O_4H^{-1}$ differ by only 1.2 kcal/mol (−5.8 vs. −7.0 kcal/mol for Reactions 8b and 8e, respectively), with the reaction with $B(OH)_4^-$ being more favorable. In fact, the difference of these two reactions is simply:

$$B(OH)_3 + OH^- \Rightarrow B(OH)_4^{-1} \quad (9)$$
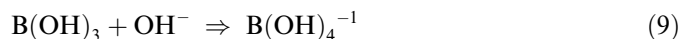
for which our calculated free energy change in aqueous solution is +1.2 kcal/mol. If the complex formed by reaction of boric acid/borate with ligand is of the form $B(OH)_2L^-$, as we have assumed, this would imply that $B(OH)_3$ would react most favorably with those ligand species with single negative charges, HL^-, e.g. $C_2O_4H^{-1}$. $B(OH)_4^-$ would react most favorably with the neutral ligand, but since the pK_a's of the dicarboxylic acid ligands lie well below the pK_a of $B(OH)_3$, the combination of a neutral H_2L dicarboxylic acid and $B(OH)_4^-$ would be impossible. $B(OH)_4^-$ does react with $C_2O_4H^{-1}$, but less favorably than with the neutral ligand.

4. Summary and conclusion

Lemarchand et al. (2005) have made a significant contribution to the atomistic characterization of humic acid by identifying a probe molecule, $B(OH)_3$, which is neutral, reacts strongly only with surface sites with well defined structural characteristics and whose complexes have readily measurable properties which are diagnostic of the local and mid-range geometric and electronic structures about the probe atom B. Fortunately, we are now able to calculate many of the properties which have been measured for these surface complexes, in order to more definitively characterize them and to establish connections between their different properties. Although these is no initial assur-

ance that $B(OH)_2L^-$ complexes in solution will be good models for related surface complexes on humic acid, both the similarity of experimental properties in the two regimes (e.g. very similar ^{11}B NMR shifts for aqueous complexes and surface complex models) and good agreement of calculated properties for gas-phase species with experimental values for surface complexes, supports the idea that the gas-phase, aqueous and surface complexes must be quite similar.

Using free $B(OH)_2L^-$ anions as models for the surface complexes and employing state-of-the-art quantum mechanical methods for evaluation of their properties leads to ^{11}B NMR shifts and δ 11B values which are in good agreement with the direct experimental results of Lemarchand et al. (2005) and with many of the fitted features of their surface models. One significant disagreement is in the magnitude of difference between the measured δ 11B values of the complexes and those assumed for $B(OH)_4^-$. This discrepancy arises from the use of an inaccurate value for the equilibrium isotopic 11B,10B fractionation constant for the $B(OH)_3$, $B(OH)_4^-$ pair (Kakihana et al., 1977), which should be replaced by the new directly determined experimental value (Byrne et al., 2006; Klochko et al., 2006), which gives a considerably more negative value for δ 11B of $B(OH)_4^-$ (δ) 11B of $-28\permil$ to $-30\permil$ at 25 °C, one much closer to the isotopic fractionations measured by Lemarchand et al. (2005). With this correction it becomes clear that the slightly different B structural environments in the BIV type $B(OH)_2L^-$ complexes, compared to $B(OH)_4^-$ itself, lead to only slightly different values of B NMR shift and 11B,10B isotopic fractionations.

Our overall results indicates that absorption of B on humic acid at relatively low pH (4 and 5) must come from the interaction of $B(OH)_3$ with partially deprotonated dicarboxylic acids like malonic acid for which 1st pK_a's would be around three in the isolated molecule. Such a malonic acid complex would give $\sigma^B = +1.5$ and would have a $\log K$ of about $+0.4$. In the same pH region a complex could be formed with α-hydroxy carboxylic acids, like glycolic acid, with $\sigma^B = +5.4$ and a $\log K$ of $+1.3$. The increase in B adsorption around pH 8–10, to a value roughly 40 times larger than that at pH 4, could be associated with a larger K value for $B(OH)_4$- than for $B(OH)3$ in reaction with the dicarboxylic acid and the α-hydroxy carboxylic acid sites but an additional contribution could come from complex formation with diphenols like catechol, which forms a $B(OH)_2L_-$ complex with $\sigma^B = +6.5$ and has a $\log K$ for formation from $B(OH)_3$ of about $+5.6$.

We have also speculated that the incorporation of B impurities into calcite may proceed through the formation of surface complexes like $B(OH)_2CO_3^-$, rather than through a simple replacement of one anion by another. Additional experimental data and more comprehensive theoretical studies will be needed to test this hypothesis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.08.014.

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