Figure 1. Distribution of ferrous complexes as a function of p[H] in a solution containing 1.14×10^{-3} M Fe(II), 1.19×10^{-3} M SHBED, and, initially, 4.75×10^{-3} M H⁺. $t = 25.00$ °C; $\mu = 0.100$ M (KNO₃).

ligand protonation constants are given in Table I.

Protonation constants of SHBED and chelate stability constants involving several metals, including the Fe^{3+} ion, were reported by Taliaferro and Martell,[8] but the ferrous ion was not studied. By application of the same anaerobic methodology used in the study of the ferrous–EDTA system for the ferrous–SHBED system, a p[H] profile was obtained that showed the formation of two protonated forms of the chelate, $FeHL^{3-}$ and FeH_2L^{2-}, stable in acid solution, and the "normal" chelate, FeL^{4-}, in which all donor groups of the ligand are deprotonated. Here also, there was no evidence for the formation of hydroxo complexes at high pH. The equilibrium constants obtained for this system are given in Table I. The mono- and diprotonated forms of the SHBED complexes are without doubt species in which one and two phenolate donor groups, respectively, are protonated and are thus not coordinated to the metal ion. In this respect the Fe(II) complexes of SHBED are analogous to its Co(II), Ni(II), and Cu(II) complexes.[8]

The species distribution curves for the ferrous–EDTA and ferrous–HEDTA systems, calculated with program SPE,[9] were featureless, with 100% formation of the 1:1 complexes, FeL^{2-} (for EDTA), and FeL^- (for HEDTA) from about p[H] 4 to 12. The species distribution curves of the Fe(II)–SHBED system however, show more complex behavior, with the major species up to pH 6 being the di- and monoprotonated complexes, as indicated in Figure 1.

The evidence presented in this paper, indicating normal behavior of the ferrous–EDTA and ferrous–HEDTA complexes, in contrast to previous literature reports,[1,3] shows the importance of rigorous exclusion of oxygen when potentiometric measurements of ferrous complexes are being carried out. Apparently a relatively small degree of contamination with air is sufficient to convert the ferrous complexes to the ferric forms.

With the corrected values for the stability constants of the Fe(II) complexes provided in this paper, assuming that the corresponding stability constants of the Fe(III) complexes are correct, it is possible to calculate the variation of reduction potentials with p[H] for these complex systems, for comparison with measured values and for correlation with their effectiveness as reducing agents. The ferrous complexes described in this paper have been employed for the reduction of a number of cobalt dioxygen complexes, which will be described in a separate publication.[10]

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Ab Initio Study of a 32-Boron Cluster: B₃₂H₃₂²⁻

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The boron hydrides B_nH_m are central to cluster chemistry. They have been used as models for the bonding in main-group and transition-metal clusters and exhibit in its simplest form the link between geometric and electronic structure.[1,2] As is well-known,[1b] the structures of the boranes may be notionally derived from the closo borane anions $B_nH_n^{2-}$, a set of deltahedral parent species that terminates experimentally with the icosahedral $B_{12}H_{12}^{2-}$. Apart from the neutral B_4H_4 (represented by its perchloro derivative, B_4Cl_4) the closo molecules have $(n + 1)$ skeletal bonding pairs and bear a charge of −2.

Though the largest known closo borane has a skeleton of 12 atoms, there has been some discussion of the possibility that even larger cages may be stable.[3-5] One such, the omnicapped dodecahedral $B_{32}H_{32}$ species, is the subject of this paper. It is the first possible I_h deltahedron after B_{12}, and its high symmetry makes an all-electron ab initio treatment of the electronic structure feasible with current programs and computer technology.

Lipscomb and co-workers[3,4] invented plausible structures for the hypothetical 13- to 24-atom clusters and speculated on the stability of a 32-boron cage. Using the semiempirical PRDDO (partial retention of diatomic differential overlap) method, they predicted electron counts for clusters with up to 24 boron atoms and found a charge of −2 to be appropriate in most cases. The exceptions were later explained by a group-theoretical argument,[5,6] clusters of T, T_d, C_3, or C_{3v} symmetry with one boron on the C_3 axis have n or $(n + 2)$ but not $(n + 1)$ skeletal bonding MOs. A recent paper[7] notes that this category would also include the hypothetical closo borane with 28 boron atoms.

$B_{32}H_{32}$ was too large for the PRDDO program,[4b] but a qualitative extended Hückel treatment[5] indicates an accidental degeneracy at the nonbonding level from which charges of +4, −2, or −8 might be deduced. In this paper we have carried out minimal basis ab initio SCF calculations to resolve the question of the appropriate charge, to find if possible the ground electronic configuration, to predict the geometric parameters of the cage, and to make an estimate of its stability.

The calculations also have a technical interest in that they show it is possible with efficient use of symmetry to perform calculations on quite large systems, thereby testing simpler models of bonding and giving preliminary data on species that may be synthesized in the future. A new version of the SYSMO molecular orbital program[8] was used, one which is adapted to take full advantage of icosahedral symmetry. Even the minimal STO-3G basis for this molecule requires 192 contracted Gaussian functions and in principle gives rise to ~172 million two-electron integrals; I_h symmetry reduces the integral total to ~1.5 million, of which only ~1.1 million are larger than the chosen cutoff value of 10^{-10} au. The symmetry reduction factor is approximately equal to the order of the group (120 for I_h), and as it affects the number of integrals to be computed, stored, and then repeatedly read during the SCF procedure, it is decisive in making the calculation possible.

In view of the recent upsurge of interest in carbon clusters,[9] it may be noted that each boron skeleton B_n for $n \geq 14$ is the dual of a possible carbon cage C_{2n-2} and that B_{32} itself is the dual of the proposed C_{60} molecule. Calculations on carbon clusters have been carried out with the present program and will be reported elsewhere.

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Table I. SCF Energies for Electronic Configurations of $B_{32}H_{32}{}^q$ at the Geometry Taken from Ref 4b: $R_{77} = 1.91$ Å, $R_{67} = 1.84$ Å, $R_{BH} = 1.19$ Å

total charge, q	confign	E_{SCF}, au
+4	$...(H_g)^{10}$	−796.24089
−2	$...(H_g)^{10}(T_{1g})^6$	−797.76886
−2	$...(H_g)^{10}(T_{1u})^6$	−797.76853
−8	$...(H_g)^{10}(T_{1g})^6(T_{1u})^6$	−794.51212

Table II. Variation of the SCF Energy of $B_{32}H_{32}{}^{2-}$ with the Geometry of the Cage[a]

R_{67}	R_{77}	$E(ec2)$	$E(ec3)$	Δ
1.84	1.84	−797.54807	−797.57347	−0.691
1.84	1.91	−797.76886	−797.76853	+0.009
1.84[b]	1.98[b]	−797.87966	−797.86215	+0.476
1.84	2.05	−797.84109	−797.80987	+0.850
1.77	1.98	−797.85610	−797.78559	+1.919
1.91	1.98	−797.64691	−797.67684	−0.814

[a] R values are given in angstroms. Energies are given in atomic units for the two electronic configurations ec2 (where the HOMO is T_{1g}) and ec3 (where the HOMO is T_{1u}). Δ is the energy difference between configurations expressed in electronvolts; a positive value of Δ implies a $...(T_{1g})^6$ ground electronic configuration. [b] These values represent the grid point nearest the optimal geometry.

Electron Count

The postulated I_h $B_{32}H_{32}$ cluster has 20 seven-coordinate boron atoms arranged at the vertices of a dodecahedron, capped by an icosahedral array of 12 six-coordinate atoms. The 32 BH bonds are radial. The geometry is determined by four parameters: R_{77} (the side of the dodecahedron), R_{67} (the side of the capping pentagonal pyramids), and the BH bond lengths R_{6H} and R_{7H}. From group-theoretical tables[10] the likely electronic configuration is deduced as follows. Each set of 32 s orbitals on B or H spans the reducible representation

$$\Gamma_\sigma = 2A_g + G_g + 2H_g + 2T_{1u} + 2T_{2u} + G_u \qquad (1)$$

and the B 2p orbitals span $\Gamma_\sigma + \Gamma_\pi$, where

$$\Gamma_\pi = 2T_{1g} + T_{2g} + 2G_g + 3H_g + 2T_{1u} + T_{2u} + 2G_u + 3H_u \qquad (2)$$

Thus the 1s cores on B and the 32 exo BH bonds span $2\Gamma_\sigma$, leaving three lobes per B for use in skeletal bonding. The dodecahedron is an electron-precise structure and its edges span

$$\Gamma_{30} = A_g + G_g + 2H_g + T_{1u} + T_{2u} + G_u + H_u \qquad (3)$$

The frontier orbitals of the 12 capping BH units span

$$\Gamma_{cap} = A_g + T_{1g} + G_g + 2H_g + 2T_{1u} + T_{2u} + G_u + H_u \qquad (4)$$

with the result that the 30 dodecahedral bonding orbitals are stabilized by capping and some new bonding MOs may also appear: Γ_{cap} contains T_{1g}, absent from Γ_{30}, and an extra T_{1u} set of orbitals. These two sets ($T_{1g} + T_{1u}$) are found to be almost exactly nonbonding in a qualitative calculation.[5] Four likely electronic configurations are therefore

$q = +4$: $\Gamma_{occ} =$
$5A_g + 3G_g + 6H_g + 5T_{1u} + 5T_{2u} + 3G_u + H_u$ (ec1)

$q = -2$: $\Gamma_{occ} =$
$5A_g + T_{1g} + 3G_g + 6H_g + 5T_{1u} + 5T_{2u} + 3G_u + H_u$ (ec2)

$q = -2$: $\Gamma_{occ} =$
$5A_g + 3G_g + 6H_g + 6T_{1u} + 5T_{2u} + 3G_u + H_u$ (ec3)

$q = -8$: $\Gamma_{occ} =$
$5A_g + T_{1g} + 3G_g + 6H_g + 6T_{1u} + 5T_{2u} + 3G_u + H_u$ (ec4)

or (ec1), (ec1)$(T_{1g})^6$, (ec1)$(T_{1u})^6$, and (ec1)$(T_{1g})^6(T_{1u})^6$.

SCF calculations were carried out for each electronic configuration at the geometry suggested by Brown and Lipscomb[3] (R_{67} = 1.84 Å, R_{77} = 1.91 Å, $R_{BH} = R_{6H} = R_{7H} = 1.19$ Å). This required a total of 12.2 h of cpu on a CONVEX C1 minisupercomputer. The results are shown in Table I and give a clear

prediction that the $B_{32}H_{32}$ species is most stable when it has a charge of −2. The highly charged +4 cation and the −8 anion are much less stable than the two dianion configurations. It is hardly surprising that an anion with a charge of 8 should be unstable; of the 100 occupied orbitals, 68 have positive eigenvalues in this STO-3G basis. Both dianion configurations have a single positive eigenvalue for the triply degenerate HOMO ($\epsilon(T_{1g})$ = +0.0868 E_h for ec2, $\epsilon(T_{1u})$ = +0.0883 E_h for ec3).

A HOMO with a positive eigenvalue is found for small closo boranes[11,12] (and for many other double negative ions such as O^{2-}). It is a symptom of the general instability of dianions with respect to singly charged or neutral species in the gas phase.[11] In a solid or in aqueous solution the dianion is preferentially stabilized by crystal-field or solvent effects, hence the existence of closo borohydride salts. When, as in the present work, we discuss the appropriate charge for a borane, it is always in the context of a properly stabilized lattice ion rather than the free species.

Studies with split-valence sets[11,13] have shown that the number and size of positive eigenvalues are exaggerated by minimal basis sets.[11] $B_6H_6{}^{2-}$ has two triply degenerate positive eigenvalues among the occupied orbitals in the STO-3G basis but only one in split-valence and larger sets;[11] $B_{12}H_{12}{}^{2-}$ has a 4-fold degenerate HOMO with a positive eigenvalue in STO-3G,[13] but in the larger 6-31G basis the eigenvalue has become a small negative quantity.[11] The HOMO becomes more bound with increasing cluster size, and so we suspect that the HOMO eigenvalue of $B_{32}H_{32}{}^{2-}$ will be found to be small and negative in a calculation in a larger basis. Free $B_{32}H_{32}{}^{2-}$ is still likely to be unstable against electron loss to $B_{32}H_{32}{}^-$ or $B_{32}H_{32}$.

One question left unresolved by Table I is the precise electronic configuration of the −2 ion. Energies in the STO-3G basis are several atomic units above the Hartree–Fock limit, and the energy difference between $(T_{1g})^6$ and $(T_{1u})^6$ configurations of 3.3 × 10^{-4} E_h (or 9 meV) could easily be reversed in a larger basis set or with a higher level of theory. Most importantly, the difference may be sensitive to the molecular geometry. The bond lengths used in Table I are based on a guess by Brown and Lipscomb.[3] To gain further understanding of the electronic structure, it is necessary to obtain a better estimate of the equilibrium geometric structure.

Geometry

A full optimization of the geometry of $B_{32}H_{32}{}^{2-}$, even in the minimal basis set, would be very costly. However, the total energy and the orbital ordering should be more sensitive to the two boron cage distances and relatively insensitive to the lengths of the BH bonds. A partial optimization of the two parameters R_{67} and R_{77} was therefore carried out, evaluating the SCF energies of both configurations of $B_{32}H_{32}{}^{2-}$ for each of five additional I_h geometries. All BH bond lengths remained fixed at 1.19 Å. The results are listed in Table II. Each point required ~6.5 h cpu on a CON-

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VEX C1. Variation of R_{77} with R_{67} fixed leads to a minimum energy for both configurations in the region of R_{77} = 1.98 Å (2.00 Å for ec2 and 1.99 Å for ec3). Fixing R_{77} to this value and allowing R_{67} to vary give a minimum at 1.87 Å for ec2 and 1.85 Å for ec3. Thus the two potential surfaces have minima in the same region of coordinate space, close to the grid point at R_{67} = 1.84 Å, R_{77} = 1.98 Å.

In the region of the minima the $(T_{1g})^6$ configuration is predicted to lie below $(T_{1u})^6$ by ~0.5 eV. The separation is probably quite sensitive to improvements in basis set, but such a small energy difference also suggests that interaction between the two configurations may be important. Until a CI calculation in a large basis set becomes possible for this system a definite assignment of configuration will remain elusive.

It is interesting that the predicted ground-state configuration disagrees with the simplest qualitative model of borane bonding—the tensor surface harmonic (TSH) theory of Stone.[14] In TSH theory a closo borane is treated as a spherical cluster and predicted to have $(n + 1)$ skeletal bonding MOs, of which one is totally symmetric and the others span the symmetries of the even vector spherical harmonics. Descent in symmetry gives a T_{1u} HOMO and a T_{1g} LUMO, i.e. configuration ec3 rather than the ec2 found in the ab initio calculations. However, more detailed qualitative calculations based on EH[15] or "structural"[16] extensions of TSH agree with the minimal-basis SCF result. The structural TSH theory[16] predicts that at high cluster nuclearity the even and odd vector spherical harmonics cross over in energy, with even (π) orbitals becoming antibonding and odd ($\bar{\pi}$) orbitals becoming bonding. In $B_{32}H_{32}^{2-}$ the T_{1u} HOMO has a $\bar{\pi}$ spherical parentage[5] so that our SCF results verify that such a crossover can indeed occur.

The bond lengths R_{67} = 1.87 Å and R_{77} = 2.00 Å represent a near-optimal geometry within icosahedral symmetry for this molecule, with boron atoms lying on or inside a sphere of radius ~3.0 Å. The whole molecule including H atoms has a radius of ~4.2 Å. Calculations in the STO-3G basis can give useful estimates of boron–boron distances. For example, the STO-3G-optimized geometry[17,18] for $B_6H_6^{2-}$ has R_{BB} = 1.68 Å compared with the experimental bond length of 1.69 ± 0.01 Å for the ion in its tetramethylammonium salt.[19] Results for larger borane cages, which have more atoms to share the "excess" negative charge, may be even better, but in any case our estimated R_{67} and R_{77} are probably accurate to ±0.03 Å.

Stability

Lipscomb and coworkers[4,12] proposed that the absolute value of the energy per BH unit, $\bar{E} = |E_{SCF}|/n$, should be used as a criterion of relative stability for closo boranes $B_nH_n^{2-}$. At the grid point nearest the optimal geometry the STO-3G basis give $\bar{E}$-$(B_{32}H_{32}^{2-})$ = 24.934 E_h. This may be compared with the value for $B_6H_6^{2-}$ at the fully optimized geometry for the same basis:[17,18] $\bar{E}(B_6H_6^{2-})$ = 24.898 E_h. $\bar{E}$ for $B_{12}H_{12}^{2-}$ at the experimental geometry (R_{BB} = 1.77 Å, R_{BH} = 1.07 Å) and in the same basis[13] is $\bar{E}(B_{12}H_{12}^{2-})$ = 24.954 E_h. On this criterion, therefore, a $B_{32}H_{32}^{2-}$ anion would be intermediate in stability between these two known species, a hopeful sign for its possible synthesis.

Registry No. $B_{32}H_{32}^{2-}$, 113249-16-4.

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Spectroelectrochemical Studies of High-Valent Nitridomanganese Porphyrins

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The reactivity of synthetic high-valent metalloporphyrins that model the active site of cytochrome P-450 has received considerable interest.[1–6] High-valent oxomanganese and oxoiron porphyrins have been described as intermediates in the catalytic transfer of oxygen from iodosylbenzene, peroxybenzoic acids, or amine *N*-oxides to numerous substrates including hydrocarbons. Recently, nitridochromium and nitridomanganese porphyrins have been prepared by Buchler,[7] Hill,[8] and Groves.[9] Remarkably, the nitrido metalloporphyrins are thermally and chemically stable. This is especially interesting since the N≡Mn core is isoelectronic with O=Fe, the reactive moiety involved in the oxygen atom transfer chemistry of the native enzyme and synthetic models.

The impetus for this study was twofold. First, we sought to place nitridomanganese porphyrins within the general framework of manganese porphyrin electrochemistry as established by Kadish.[10] Second, we hoped to electrochemically activate the N≡Mn^V moiety and exploit its chemistry. The spectroelectrochemical results presented herein show that although we were unable to activate the N≡Mn^V moiety electrochemically, the redox reactivity of nitridomanganese porphyrins is unique when compared with that of other manganese porphyrins.

Experimental Section

Several high-valent manganese porphyrins[13] were synthesized from the corresponding manganese (III) porphyrins (previously prepared accord-

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