the use of a low-cost, nontoxic, commercially available starting material, and (iv) a simple, one-step process giving a pure product in high yield.

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Ferrous Chelates of EDTA, HEDTA, and SHBED

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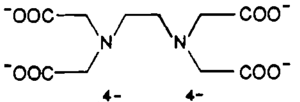
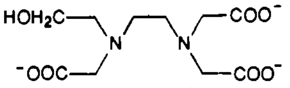
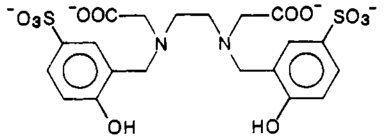
In the course of investigating the kinetics of reduction of several dioxygen complexes by iron(II) chelates of EDTA (**1**, ethylenediamine-*N,N'*-tetraacetic acid), HEDTA (**2**, *N*-(hydroxyethyl)ethylenediamine-*N,N'*-triacetic acid) and SHBED (**3**, *N,N'*-bis(2-hydroxy-5-sulfobenzyl)ethylenediamine-*N,N'*-diacetic acid),



1^{4-}, $EDTA^{4-}$



2^{3-}, $HEDTA^{3-}$



3^{4-}, $SHBED^{4-}$

it was found that the reduction potentials of the ferrous chelates of EDTA and HEDTA do not vary with p[H] in the manner predicted by the equilibrium data in the literature. The hydrolysis constants of Fe(II)-EDTA reported by Schwarzenbach and Heller[1] (pK = ca. 9.1), together with the well-known hydrolysis constant of Fe(III)-EDTA[2] (pK = ca. 7.5) indicate that in a pH range where the monohydroxo forms of both Fe(II) and Fe(III) chelate compounds exist, the reduction potential should not vary very much with p[H]. The fact that this was found not to be the case led to the idea that the equilibrium data for Fe(II)-EDTA may be in error. This interpretation is reinforced by the fact that the hydrolysis constants published for the formation of $Fe(OH)L^{3-}$ and $Fe(OH)_2L^{4-}$ have no counterpart with the accepted equilibrium constants for the adjacent metal ions, Mn^{2+} and Co^{2+}. A hydrolysis constant of similar magnitude reported for Fe(II)-HEDTA[3] (pK = ca. 8.8) indicates that some of the other early work might also be in error. It was therefore decided to investigate these two ferrous chelate systems, along with the ferrous chelate of another ligand, SHBED, which is also being employed in our studies of the reduction of dioxygen complexes, to be reported separately.

Experimental Section

SHBED, obtained from Lyndal Chemical, was recrystallized from water acidified with acetic acid; the EDTA, HEDTA, and $FeSO_4 \cdot 7H_2O$ employed were of reagent grade quality and were used without further purification. Purity of all ligands was verified by titration with standard carbonate-free KOH. Carbonate-free 0.1 M potassium hydroxide solutions were prepared from Baker Dilut-It ampules with boiled distilled water and were standardized by titration with potassium hydrogen phthalate to a phenolphthalein end point. Gran's method[4] was used to confirm the absence of carbonate in the potassium hydroxide standard solution and the absence of atmospheric contamination of the sample during the course of potentiometric equilibrium measurements.

Table I. Protonation and Fe(II) Chelate Formation Constants of EDTA, HEDTA, and SHBED

	formation constant		
equilibrium quotient	EDTA (H_4L)	HEDTA (H_3L)	$SHBED^{2-}$ (H_4L^{2-})
[HL]/([L][H])	10.17[a]	9.82	12.27[b]
$[H_2L]/([HL][H])$	6.11[a]	5.31	10.25[b]
$[H_3L]/([H_2L][H])$	1.95[a]	2.55	8.05[b]
$[H_4L]/([H_3L][H])$	1.5[a]		4.50[b]
$[H_5L]/([H_4L][H])$			2.59[b]
$[H_6L]/([H_5L][H])$			1.80[b]
[ML]/([M][L])	14.94[c]	12.58[c]	19.75[c]
[MHL]/([ML][H])	2.06[c]	2.36[c]	6.25[c]
$[MH_2L]/([MHL][H])$			4.73[c]

[a] References 2 and 7. [b] Reference 8. [c] This work.

Equilibrium Measurements. Potentiometric measurements were performed in a jacketed, airtight glass titration cell equipped with O-ring fittings for glass and saturated calomel electrodes and for gas inlet and outlet tubes. A Teflon adapter was used to attach a microburet to this vessel.

All solutions were adjusted to 0.100 M ionic strength by addition of potassium nitrate. The temperature was maintained at 25.00 ± 0.01 °C by circulating thermostated water through the outer jacket of the cell. Solutions were kept under an atmosphere of argon that was passed through alkaline pyrogallol scrubbers to remove oxygen and carbon dioxide and then equilibrated with water vapor by passage through a 0.100 M potassium nitrate solution.

Measurements were made with a Corning Model 130 pH meter calibrated with standard acid and base so that $[H^+]$ concentration was measured directly. For the purpose of this paper the term p[H] designates the negative log of the hydrogen ion concentration.

Ligand protonation constants, K_H^n, as defined by

$$H_{n-1}L^{x+} + H^+ \rightleftharpoons H_nL^{(x+1)+} \qquad K_H^n = \frac{[H_nL^{(x+1)+}]}{[H^+][H_{n-1}L^{x+}]} \tag{1}$$

were verified by potentiometric equilibrium measurements of 1.0×10^{-3} M solution of the acid form of each ligand in the absence of metal ions. These equilibrium constants were calculated by the computer program PKAS.[5]

Acid forms of organic ligands have often been found to contain nonstoichiometric amounts of water. By a systematic variation of the molecular weight so as to minimize the difference between observed and calculated p[H] values, corrected ligand concentrations were calculated.

Equilibria in the 1:1 metal-ligand systems were found to be represented adequately by eq 2-4. The experimental solutions contained

$$M + L \rightleftharpoons ML \qquad K_{ML} = \frac{[ML]}{[M][L]} \tag{2}$$

$$ML + H^+ \rightleftharpoons MHL \qquad K_{MHL}^H = \frac{[MHL]}{[ML][H^+]} \tag{3}$$

$$MHL + H^+ \rightleftharpoons MH_2L \qquad K_{MH_2L}^H = \frac{[MH_2L]}{[MHL][H^+]} \tag{4}$$

approximately 1×10^{-3} M Fe(II) and 1×10^{-3} M ligand. Potentiometric data were analyzed and the equilibrium constants were calculated with the aid of the computer program BEST.[6]

Results and Discussion

Careful potentiometric equilibrium p[H] measurements of 1:1 Fe^{2+}-EDTA and Fe^{2+}-HEDTA solutions with rigorous exclusion of oxygen gave p[H] profiles showing no indication of hydrolysis up to p[H] 12. Calculation of the equilibrium constants of these systems by the methods previously described,[5,6] gave only the formation constants of the simple 1:1 chelates and constants for the formation of monoprotonated species at low p[H]. The equilibrium constants for these complexes and the corresponding

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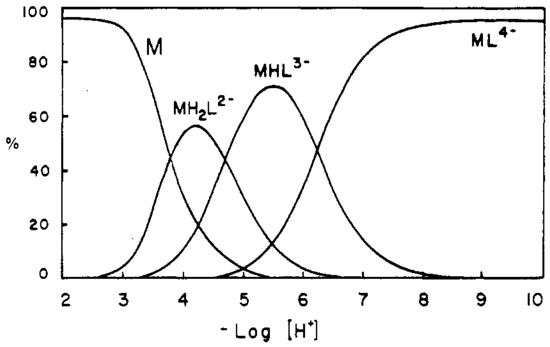

Figure 1. Distribution of ferrous complexes as a function of p[H] in a solution containing 1.14×10^{-3} M Fe(II), 1.19×10^{-3} M SHBED, and, initially, 4.75×10^{-3} M H^+. t = 25.00 °C; μ = 0.100 M (KNO_3).

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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Registry No. $FeEDTA^{2-}$, 15651-72-6; $FeHEDTA^-$, 43218-58-2; $FeSHBED^{2-}$, 112968-86-2.

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Ab Initio Study of a 32-Boron Cluster: $B_{32}H_{32}^{2-}$

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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 coworkers[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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