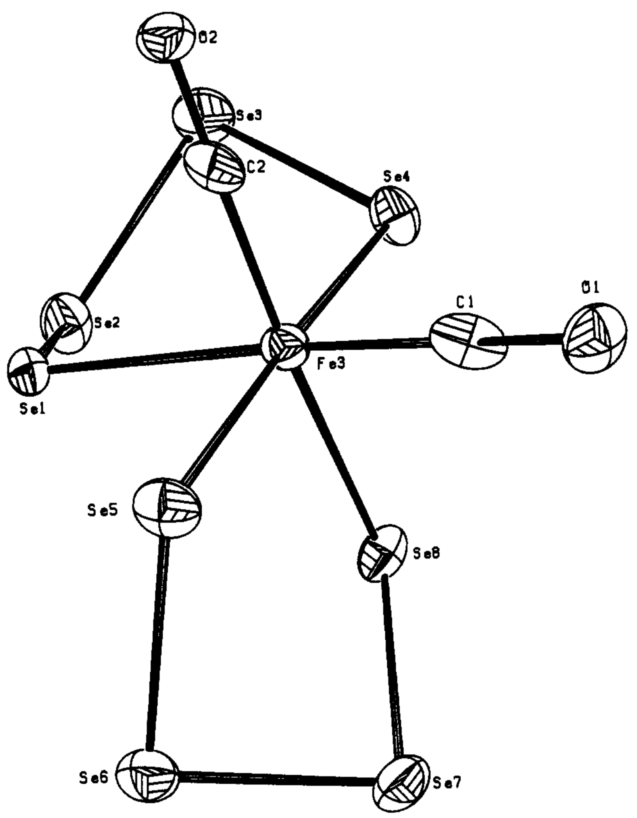

Figure 1. Structure of the anion of $[Fe(N\text{-}MeIm)_6]^{2+}[Fe(Se_4)_2(CO)_2]^{2-}$, with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å): Fe–N range = 2.17–2.21 (2); Se–Se range = 2.331–2.349 (3); Fe–Se1 = 2.450 (3); Fe–Se5 = 2.419 (3); Fe–Se8 = 2.439 (3); Fe–C1 = 1.75 (2); Fe–C2 = 1.73 (2). Selected bond angles (deg): Se5–Fe–Se8 = 99.7 (1); Se1–Fe–Se4 = 97.7 (1); C1–Fe–C2 = 94.4 (10).

1. High S:M ratios favor the *cleavage* of metal–sulfur bonds in polysulfido complexes. This is due to the fact that the basicity of S_x^{2-} is inversely proportional to x.[10]

2. Elemental sulfur is selectively Lewis acidic toward the sulfur anions. This occurs even in preference to a large excess of highly basic N-MeIm.

3. Polysulfido ligands are less capable of stabilizing high oxidation states than sulfide (S^{2-}). This is illustrated by the reduction of Fe^{III} (in $Fe_2S_{12}^{2-}$) to Fe^{II} (in $[Fe(N\text{-}MeIm)_6]S_8$). This conversion is reminiscent of the metal-centered reduction of $Mo^{VI}S_4^{2-}$ by S_8.[11]

The nature of the donor solvent influences the thioanion generated via our donor-solvent-promoted reactions of $Fe(CO)_5$ (and, more slowly, via those of Fe powder). This was demonstrated using 1,2-Me_2Im, whose coordinating power suffers because of nonbonded interactions between the 2-methyl group and adjacent ligands within an octahedral coordination sphere.[12] The reaction (50 °C, 6 h) of S_8 with a 1,2-Me_2Im solution of $Fe(CO)_5$ gave, after ether precipitation, exclusively $[Fe(1,2\text{-}Me_2Im)_6][Fe_2S_{12}]$,[13] *despite the presence of excess sulfur*. Reactivity studies relate $[Fe(1,2\text{-}Me_2Im)_6][Fe_2S_{12}]$ to all other iron compounds described herein (Scheme I).

The stability of DMF solutions of $[Fe(N\text{-}MeIm)_6]Y$ ($Y = [Fe_2S_{12}]^{2-}$, S_8^{2-}) contrasts with our finding that attempted dissolution of $[Ni(N\text{-}MeIm)_6]S_8$ in DMF results in immediate deposition of NiS.[2] The stability of DMF solutions of $[FeL_6]$(thioanion) suggests two lines for further research, synthesis of polysulfide salts of other iron cations by ligand exchange at the cation and the dissolution of iron metal in DMF/S_8.

The reactions of metal carbonyls (Mn, Fe, Ni) with N-MeIm suspensions of gray selenium also proceed well. The N-MeIm/$Fe(CO)_5$/Se reaction (25 °C, 12 h; toluene precipitation) afforded brown microcrystals of $[Fe(N\text{-}MeIm)_6]^{2+}[Fe(Se_4)_2(CO)_2]^{2-}$ in 94% yield (eq 1).[14] X-ray crystallography[15] showed that this salt

$$2Fe(CO)_5 + 8Se \rightarrow [Fe(N\text{-}MeIm)_6][Fe(CO)_2(Se_4)_2] + 8CO \qquad (1)$$

consists of pseudooctahedral $[Fe(N\text{-}MeIm)_6]^{2+}$ and $[Fe(Se_4)_2(CO)_2]^{2-}$ centers (Figure 1). The unit cell contains two different but similar centrosymmetric dications. The anion adopts a cis geometry with two $FeSe_4$ rings. Although substituted iron polychalcogenides are rare, the dianion closely resembles $[Ru(Se_4)_2(CO)_2]^{2-}$, obtained from the reaction of K_2Se_5 and $Ru_3(CO)_{12}$.[16] This similarity highlights the relationship between the reactions N-MeIm/$M(CO)_n$/Se and $M(CO)_n/E_n^{2-}$.[17] The N-MeIm/$M(CO)_n$/X reaction generates its own gegenion in the form of the very stable $[M(N\text{-}MeIm)_6]^{2+}$.

On the basis of these results, it is clear that strong donor solvents provide a powerful means to explore reactivity networks for metal polychalcogenide complexes.

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Supplementary Material Available: Tables of bond distances and angles, thermal parameters, and atomic coordinates and ORTEP diagrams of the cations (7 pages); a listing of structure factors (19 pages). Ordering information is given on any current masthead page.

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(14) Anal. Calcd for $C_{26}H_{36}N_{12}Fe_2O_2Se_8$: C, 24.17; H, 2.81; N, 13.00; Se, 48.88. Found: C, 24.13; H, 2.81; N, 12.80; Se, 49.26. Its IR spectrum (KBr) shows ν_{CO} bands at 1958 and 1911 cm^{-1}. The molar conductance of its N-MeIm solution (5.22×10^{-4} M) is 49.80 Ω^{-1} cm^{-2} mol^{-1}.

(15) Crystal grown from N-MeIm and THF: $C_{26}H_{36}N_{12}Fe_2O_2Se_8$, $P\bar{1}$, a = 9.651 (3) Å, b = 10.877 (4) Å, c = 19.697 (5) Å, α = 89.80 (2)°, β = 88.62 (2)°, γ = 83.33 (3)°, V = 2053 (2)Å^3. With Mo Kα radiation, 6257 reflections were collected at −78 °C, of which 2845 were observed ($I > 2.58\sigma(I)$). The data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods (SHELX-86) and refined to final R = 0.056 and R_w = 0.062.

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Stability and Structure of $C_{12}B_{24}N_{24}$: A Hybrid Analogue of Buckminsterfullerene

The 60-vertex, truncated icosahedral cluster system known as buckminsterfullerene ("buckyball", C_{60}), has attracted increased attention following recent reports of its laboratory-scale synthesis.[1] Such large clusters provide a bridge between atomic and ma-

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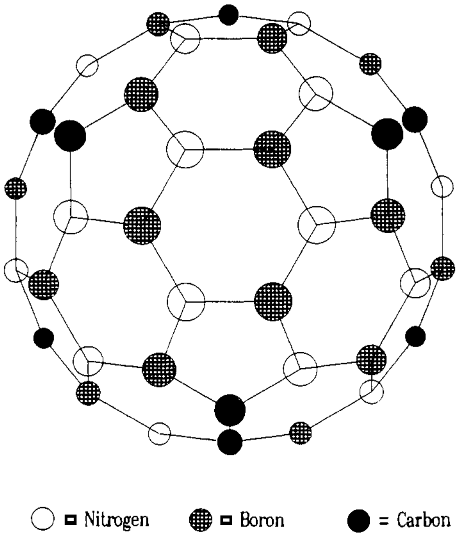


Figure 1. Structure of $C_{12}B_{24}N_{24}$ as viewed along the C_3 rotational axis. Nine of the 12 carbons (all six equatorial plus three polar) are shown.

croscopic species, and hence have considerable technological importance—for example, in electrochemistry,[2] ferromagnetism,[3] and superconductivity.[4] Various efforts to add heteroatoms (especially nucleophiles) to the periphery of C_{60} frameworks have been successful,[5] and possible structures for hydrogenated species have been discussed.[6]

Smalley and co-workers doped C_{60} with boron and nitrogen atoms, with mass spectral evidence for species such as $C_{59}B$ and $C_{58}B_2$ having been obtained.[7] The possibility of a $C_{58}BN$ cluster is especially intriguing. The isoelectronic relationship between boron–nitrogen and dicarbon molecular fragments is well documented and is manifested in a variety of ways. For example, the structural chemistry of boron nitride closely parallels that of elemental carbon—hexagonal BN (α-BN) is an analogue of graphite, while β-BN is isostructural with diamond.[8]

It is therefore reasonable to suppose that B–N analogues of buckyball will be stable. The complete replacement of carbon by B–N units would yield the $B_{30}N_{30}$ cluster. However, in that case the truncated icosahedral structure is expected to have limited stability, because it would necessarily contain relatively weak B–B and N–N bonds.[7] On the other hand, the stepwise replacement of C_2 units with BN to produce $C_{58}BN$, $C_{56}B_2N_2$, etc. is more feasible. Since for any fullerene structure there are exactly 12 pentagons, it should be possible to substitute all but 12 carbons of C_{60} with alternating boron and nitrogen atoms. The resulting cluster would have the molecular formula $C_{12}B_{24}N_{24}$, with six C–C, 12 C–B, 12 C–N, and 60 B–N nearest-neighbor interactions.

The derived structure (Figure 1) consists of six pairs of pentagons, with each pair connected by a C–C bond. The 20 hexagons subdivide into 12 $C_2B_2N_2$ and eight B_3N_3 units, each ring being isoelectronic with its all-carbon counterpart. The molecule has a single proper axis of rotation (C_3), and belongs to the S_6 point group. There are two chemically different kinds of carbon atoms—six nearer to the equator and six nearer the pole.

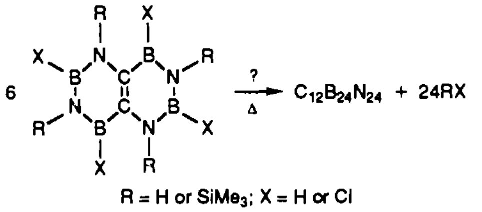
Detailed quantum calculations for a range of BN-substituted buckyball analogues are in progress. However, to estimate the stability of $C_{12}B_{24}N_{24}$, we have carried out a simple Hückel calculation of the type used by Haymet to predict the stability of C_{60} itself.[9] Each bond type (C–C, C–B, C–N, and B–N) requires a value for the resonance integral β. Assigning β(C–C) to be 1.0, we get β(B–C) = 0.7 and β(C–N) = 1.0.[10] β(B–N) was taken to be 0.9 based on the relative π-bond energies of benzene and borazine.[11] Literature values for the Coulomb integrals α are α(B) = −1.0 and α(C) = 0.0. For neutral nitrogen, values range from +0.5 to +1.5 depending on the assumed electron density.[10]

The delocalization energy is defined as the difference between the Hückel energy and that of a single resonance structure. Using the parameters listed above, we estimate the energy of the most stable Kekule structure to be −55 Hückel units (Hu), and the delocalization energy for $C_{12}B_{24}N_{24}$ is in the range of 45 ± 7 Hu. (Haymet's value for C_{60} is −33.2 Hu.[9]) We therefore conclude that $C_{12}B_{24}N_{24}$ should be stable.

All synthetic routes to buckyball involve self-assembly. The original method utilized the photofragmentation of graphite,[12] while newer techniques involve the vaporization of graphite rods or collecting soot from the controlled pyrolysis of benzene.[1] It is therefore reasonable to suppose that BN derivatives can also be self-assembled, and this is in fact how $C_{59}B$ and $C_{58}B_2$ were produced.[7]

Plausible syntheses based on thermal elimination reactions can also be suggested; such reactions have previously been used to produce structurally related fused rings, polymers, and ceramics. For example, the pyrolysis of C_2BN_2 ring compounds have been suggested as precursors for linear polymers having backbones of alternating boron and nitrogen atoms, with carbon-containing groups as substituents.[13] Borazine rings linked by organic or other moieties have been studied as precursors to high-purity boron nitride,[14] and derivatives of polyhedral boranes have been used similarly.[15]

Ideal precursors to $C_{12}B_{24}N_{24}$ would have C:B:N atomic ratios of 1:2:2. One possibility we are exploring utilizes species containing fused $C_2B_2N_2$ rings (eq 1). A synthetic route to the 1,3-diaza-2,4-diborine ring system has been described.[16] Given the ap-



$$6\,(\ldots) \xrightarrow[\Delta]{?} C_{12}B_{24}N_{24} + 24RX \qquad (1)$$

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propriate substituents, pyrolysis leading to the elimination of some small molecule (H_2, HCl, or Me_3SiCl) might reasonably lead to cluster formation.[17]

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Registry No. $C_{12}B_{24}N_{24}$, 137720-14-0.

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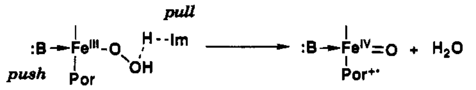
Push Effect on the Heterolytic O–O Bond Cleavage of Peroxoiron(III) Porphyrin Adducts

In the oxygen activation mechanisms by P-450, peroxidases, and catalase, a heterolytic O–O bond cleavage process of (hydroperoxo)iron(III) porphyrin complexes is believed to afford oxoferryl ($O{=}Fe^{IV}$) porphyrin cation radical intermediates.[1] In fact, the reactive species called "compound I" is observable in some peroxidase reactions.[2] For these heme enzymes, it has been proposed that the proximal ligands (thiolate,[3] imidazolate,[4] and phenolate[5]) are crucial to the heterolytic process by serving as a strong internal electron donor to destabilize the O–O bond of a (hydroperoxo)iron(III) porphyrin (*push effect*).[6] In addition, distal histidine residues in some cases are considered to serve as a general acid/general base to assist heterolytic O–O bond cleavage as shown below (*pull effect*).[6]



$$:B \rightarrow Fe^{III}(Por)\text{-}O\text{-}OH\cdots H\text{-}Im \longrightarrow :B \rightarrow Fe^{IV}(Por^{+\cdot}){=}O + H_2O \quad (1)$$

The push–pull mechanism has been examined by several model systems.[7-9] For instance, the catalytic oxidation of tri-*tert*-butylphenol by synthetic iron porphyrin complex/peracid (or hydroperoxide) systems was enhanced by added buffers and by covalently attached bases.[7] Further, Bruice et al. also reported general-acid/general-base effects by using similar catalytic systems.[8] Kinetic studies of the reactions indicate the oxidation being first order in [peracid (or hydroperoxide)] and [iron porphyrin] under the reaction conditions.[7,8] While these observations are very important to understand biological manipulation of hydrogen peroxide against the Fenton type radical process by utilizing the push–pull effects, observed second-order rate constants (k_{obs}) do not represent the O–O bond cleavage step (k_{dec}) since k_{obs} apparently includes preequilibrium constants (K_{eq}) as shown in eq

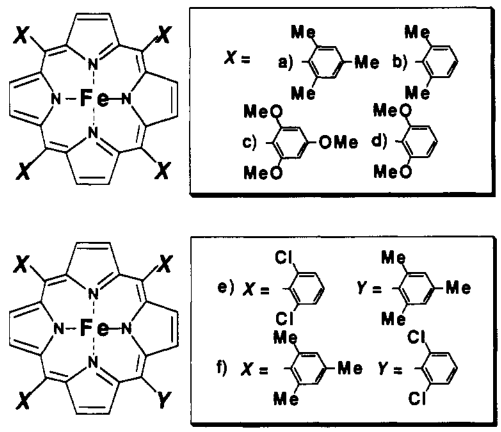


Figure 1. Structures of the porphyrin core of various substituted iron porphyrin complexes (**a–f**) employed in this study. Axial ligands have been omitted for simplicity.

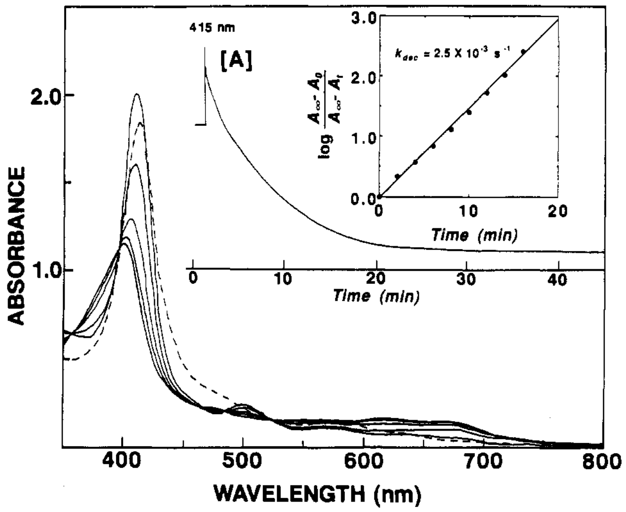


Figure 2. Visible spectral changes in the reaction of 2.0 × 10^{-5} M hydroxoiron(III) porphyrin (**3b**) and 3 equiv of *p*-nitroperoxybenzoic acid in methylene chloride at −80 °C. The spectrum of **4b** was recorded immediately after the addition of *p*-nitroperoxybenzoic acid. Line A represents the time-dependent change of absorbance at 415 nm. Inset: Plots of log $[(A - A_0)/(A - A_t)]$ at 415 nm vs time for the formation of **5b** by the reaction of **3b** with 3 equiv of *p*-nitroperbenzoic acid in CH_2Cl_2 at −80 °C.

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