Volume 31
Number 12
June 10, 1992

Inorganic Chemistry

Communications

Two Unusual Formate-Bridged Manganese(III) Tetraphenylporphyrin Complexes

Manganese porphyrin complexes have been the subject of intense scrutiny for well over 2 decades largely because of an impressive biomimetic capacity. Most notably synthetic manganese porphyrin complexes have been used very successfully as models for the cytochromes P-450.[1] A good deal of effort has accordingly been invested in the characterization of high oxidation state species found in solution,[1] and complementing these studies, a large number of solid-state structural investigations have been carried out.[2-20] As a prelude to a more complete characterization, we briefly describe here the crystal structure and spectroscopy of two novel (formato)manganese tetraphenylporphyrin complexes, $[(\mathrm{TPP})\mathrm{Mn}(\mathrm{HCO_2})]_n$ (**1**) and $[(\mathrm{TPP})\mathrm{Mn}(\mathrm{HCO_2})]_3{\cdot}6\mathrm{CHCl_3}$ (**2**), in which the manganese porphyrin moieties are linked by bridging formate ion ligands (Figures 1 and 2). These complexes have sufficient significance for metalloporphyrin coordination chemistry to warrant a prompt structural communication.

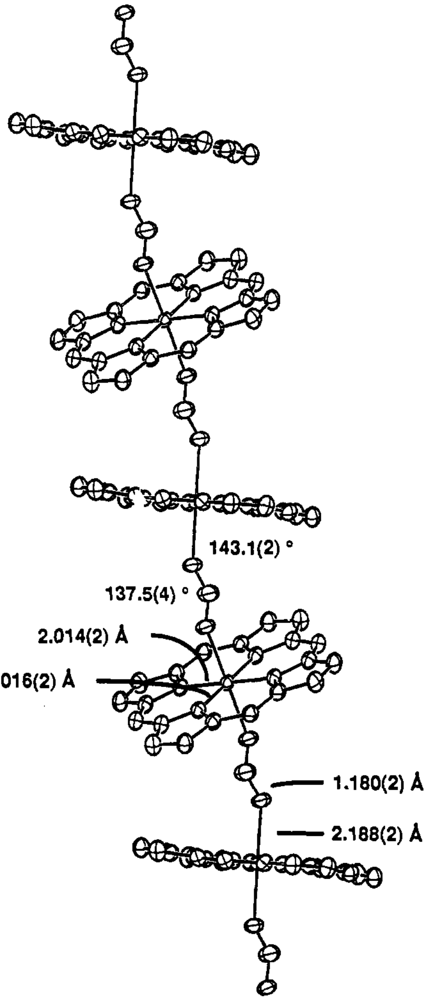

Figure 1. ORTEP plot showing five units and important metrical details of the $[(\mathrm{TPP})\mathrm{Mn}(\mathrm{HCO_2})]_n$ polymer (**1**). Each Mn(III) atom is located at an inversion center in *C*2/*c*. For the sake of clarity, *meso*-phenyl groups have been omitted.

Long dark green oblong crystals of the very unusual polymeric complex **1** were the unexpected outcome of washing a $\mathrm{CH_2Cl_2}$ solution of (TPP)Mn(Cl) several times with a 5% aqueous NaOH solution. The organic layer was separated and, using a rotary evaporator, its volume repeatedly halved and then doubled by the addition of THF. Finally, heptane was allowed to slowly infuse into the resultant solution over several weeks. Groves and Stern[21] have found that in $\mathrm{CHCl_3}$, manganese porphyrins aerobically react with hydroxide ions to generate a dichlorocarbonyl oxide species which leads to the generation of a reactive oxomanganese(IV) porphyrin complex. Additionally, Arasasingham and Bruice[22] have shown that peroxomanganese porphyrin complexes can be formed from the aerobic reaction of hydroxide ions with manganese porphyrins in organic solvents. Model P-450 alkane hydroxylations catalyzed by manganese porphyrins[23] in $\mathrm{CHCl_3}$ or $\mathrm{CH_2Cl_2}$ solvents

---

(1) Gunter, M. J.; Turner, P. *Coord. Chem. Rev.* **1991**, *108*, 115.
(2) Williamson, M. M.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 4155.
(3) Williamson, M. M.; Hill, C. L. *Inorg. Chem.* **1986**, *25*, 4668.
(4) Hill, C. L.; Williamson, M. M. *Inorg. Chem.* **1985**, *24*, 2836.
(5) Hill, C. L.; Williamson, M. M. *Inorg. Chem.* **1985**, *24*, 3024.
(6) Hatano, K.; Anzai, K.; Iitaka, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 422.
(7) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301.
(8) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *Am. Chem. Soc.* **1982**, *104*, 3964.
(9) Landrum, J. T.; Reed, C. A.; Hatano, K.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3232.
(10) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 3776.
(11) Day, V. W.; Stults, B. R.; Tasset, E. L.; Day, R. O.; Marianelli, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 2651.
(12) Kirner, J. F.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 2081.
(13) Tulinsky, A.; Chen, B. M. L. *J. Am. Chem. Soc.* **1977**, *99*, 3647.
(14) Suslick, K. S.; Watson, R. A.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 2311.
(15) VanAtta, R. B.; Strouse, C. E.; Hanson, L. K., Valentine, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 1425.
(16) Suslick, K. S.; Watson, R. A. *Inorg. Chem.* **1991**, *30*, 912.
(17) Kirner, J. K.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 1093.
(18) Day, V. W.; Stults, B. R.; Tasset, E. L.; Marianelli, R. S.; Boucher, L. J. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 305.
(19) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J. A.; Scheidt, W. R. *Inorg. Chem.* **1983**, *22*, 888.
(20) Scheidt, W. R.; Lee, Y. J.; Luangdilok, W.; Haller, K. J.; Anzai, K.; Hatano, K. *Inorg. Chem.* **1983**, *22*, 1516.
(21) Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1988**, *110*, 8628.
(22) Arasasingham, R. D.; Bruice, T. C. *Inorg. Chem.* **1990**, *29*, 1422.
(23) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374.

0020-1669/92/1331-2295$03.00/0 © 1992 American Chemical Society

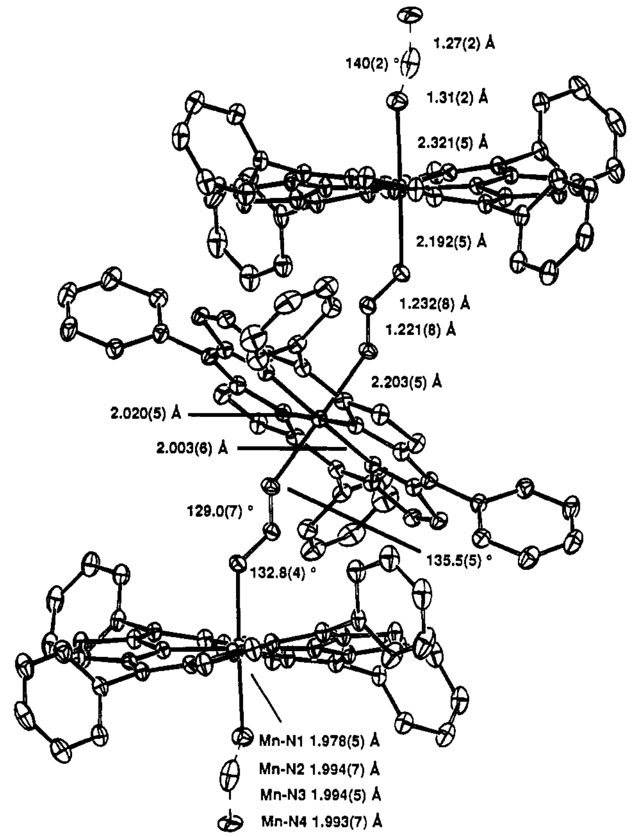

Figure 2. ORTEP plot and associated details of the $[(TPP)Mn(HCO_2)]_3{\cdot}6CHCl_3$ complex. The central manganese is located on an inversion center in $P\bar{1}$ whereas the second independent manganese ion resides on a general position. The broken bond links the sites 50% occupied by H_2O and HCO_2^-.

produce high yields of halogenated alkane side product arising from oxidative solvent decomposition. Thus it is reasonable to conclude that the formato polymer **1** is a product of solvent oxidation.

The unprecedented trimeric manganese porphyrin complex **2** was prepared by dissolving so-called "(TPP)Mn(OH)"[20] in methanol and adding an equivalent of formic acid. Diffraction quality crystals were obtained by stripping the solvent, redissolving in freshly distilled $CHCl_3$, filtering, allowing hexane to infuse until crystals began to deposit at the solution surface, and then leaving the solution to stand overnight. The very dark green crystals so obtained rapidly lost solvent and had to be mounted in a thin-walled capillary for X-ray diffraction data collection.

The IR spectrum of **1** in Nujol shows a composite carbonyl band centered at 1600 cm^{-1} ascribed to an asymmetric stretch of the formate ligand. The principal difference between the IR spectrum in Nujol of complex **2** and that of **1** is the appearance of a weak band at 1280 cm^{-1}, which seems likely to be a symmetric stretch of the terminal formate ligand (a $\Delta\nu$ of 320 cm^{-1} is typical for a unidentate carboxylate[24]). In chloroform solution both **1** and **2** can reasonably be expected to be monomeric, and the strong carbonyl band of the formato manganese porphyrin appears at 1612 cm^{-1}, with the weaker symmetric stretch at 1307 cm^{-1} (the intense carbonyl band appears at 1626 cm^{-1} in CH_2Cl_2). The optical spectrum in dichloromethane is typical of a d-type hyperporphyrin[25] and has band V at 472 nm and a $\epsilon(V)/\epsilon(VI)$ ratio of 2.52, indicating that the formate-coordinated manganese valence level is above the porphyrin LUMO level. The ^1H NMR spectrum in $CDCl_3$ resembles those of other manganese(III) porphyrin complexes[26,27] and a pyrrole β-proton isotropic shift of 34.55 ppm is similar to the 31.05 ppm shift in (TPP)Mn(Cl).

The structure of **1** (Figure 1)[28] is built up from (tetraphenylporphinato)manganese(III) complexes linked by formate ligands, with one half of the formula unit comprising the asymmetric unit of the structure. The manganese atom lies on a crystallographic inversion center, and the formate carbon atom sits on a 2-fold axis, as does the THF oxygen atom. The porphyrin skeleton is close to planar with the largest non-hydrogen atom deviation being 0.074 Å. The formate plane and the O–Mn–O axis make angles of 96.02 (6) and 87.077 (5)° with the porphyrin plane, respectively. The Mn–O(formate) bond length, 2.188 (2) Å, is, as expected, shorter than the 2.271 (2) Å reported[2] for Mn–O(water) in $[(TPP)Mn(H_2O)_2]ClO_4$. The Mn–N bond lengths are not significantly different (Figure 1). The -Mn-Mn-Mn- axes of four chains of the linked porphyrin complexes run parallel to *c* and stretch across four sides of the unit cell; one chain runs between the points (0.5, 0, 0) and (0.5, 0, 1), another between (0.5, 1, 0) and (0.5, 1, 1), a third between (0, 0.5, 0) and (0, 0.5, 1), and the fourth between (1, 0.5, 0) and (1, 0.5, 1). The polymer chains are stacked directly on top of one another in the *b* direction to form layers stacked in the *a* direction. Alternate layers are displaced by half the length of the *b* axis (i.e. 6.623 Å) in the direction of that axis. The chains within a layer are formally separated by the length of the *b* axis, 13.265 (3) Å, and the distance between chains in adjacent layers is 13.707 Å. Complex **1** has parallel chains throughout and so differs fundamentally from $[(TPP)Mn(imidazolate)]_n$, the other manganese porphyrin polymer reported to date,[9] which is comprised of alternating layers having orthogonal chain directions. The intrachain Mn–Mn distance of **1** is 6.414 Å compared to 6.54 Å for $[(TPP)Mn(imidazolate)]_n$.

Phenyl residue contacts are minimized in the achiral chain, by an alternating ±29.75° rotation of consecutive porphyrin ligands around the -Mn-Mn- chain axis. Additionally, the ligands are tilted with respect to the chain axis so as to form an angle of 72.18° with this axis and the dihedral angle between adjacent planes along the chain is then 34.94°. As a result of this geometry, the shortest distance between sites on adjacent chains in a given layer, is 3.907 Å between a phenyl meta carbon site and a pyrrole β-carbon site. In contrast, the shortest distance between sites on chains in adjacent layers is 3.483 Å between a phenyl ortho and a phenyl meta carbon position. The partially occupied and disordered solvent and water sites are located in cavities formed by the ligand planes of the polymer chains.

Some rotational disorder of the formate bridge about the Mn–Mn axis, suggested by high thermal motion of the formate carbon in the *x* direction (perpendicular to the formate plane; U_{11} = 0.132 (5) Å^2, U_{22} = 0.058 (3) Å^2, U_{33} = 0.050 (3) Å^2), is probably responsible for the short C–O bond length, 1.180 (2) Å, the large Mn–O–C angle of 143.1 (2)°, and the large O–C–O angle of 137.5 (4)° (cf. 1.25 Å and 120° reported[24,29] for the formate-bridged $Cu(HCO_2)_2{\cdot}4H_2O$; the C–O bond length in CO_2 is 1.16 Å[24]). Alternatively or additionally, the bridging formate geometry may suggest a nontrivial level of sp hybridization of the formate carbon and oxygen atoms, and this in turn would indicate a significant π interaction between the bridge and metal ions.

Disorder is not apparent in the bridging formate ions of the trimeric complex **2**,[30] shown in Figure 2, in which the C–O bond

---

(24) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, Chapter 15.6.

(25) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed., Academic Press: New York, 1979; Vol. III, Chapter 1.

(26) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1975**, *97*, 5103.

(27) Turner, P.; Gunter, M. J. submitted for publication in *Inorg. Chem.*

(28) $[(TPP)Mn(HCO_2)]{\cdot}THF{\cdot}H_2O$, $C_{49}H_{39}N_4O_4$: M = 802.82; very dark green, monoclinic, space group $C2/c$, a = 23.991 (5) Å, b = 13.265 (3) Å, c = 12.831 (3) Å, β = 98.60 (2)°; V = 4037.3 Å^3, D_c (Z = 4) = 1.321 g cm^{-1}, T = 294 K; crystal dimensions 0.35 × 0.23 × 0.16 mm, μ(Mo Kα) = 3.30 cm^{-1} (no correction); Enraf-Nonius CAD-4 diffractometer, λ(Mo Kα, graphite monochrometer) = 0.7107 Å, $F(000)$ = 1672 electrons; N(θ_{max} = 25°; ω/θ mode) = 3203, $N_o(I > 2.5\sigma(I))$ = 2584, number of variables = 360; range of *hkl* ±28, 0 to 15, 0 to 15; R = 0.036, R_w = 0.040, residual extrema 0.18, −0.22 e Å^{-3}; heavy atom solution with SHELX-76 program suite; anisotropic thermal parameters refined for the non-hydrogen atoms with (x, y, z, U_{iso}) refined for hydrogen atoms; neutral atom scattering factors; no extinction. The nature of the THF disorder about the 2-fold axis could not be delineated.

(29) Kiriyama, R.; Ibamoto, H.; Matsuo, K. *Acta Cryst.* **1954**, *7*, 482.

lengths of the formate link are 1.220 (8) and 1.232 (8) Å, the Mn–O–C angles are 135.5 (5) and 132.8 (4)° and the O–C–O angle is 129.0 (7)°. However in the centrosymmetric model adopted, in space group $P\bar{1}$, the terminal axial coordination sites of **2** are 50% occupied by H_2O and HCO_2^-, and this is likely to influence to some extent the apparent metal–bridge interaction and bridge geometry of **2**. The bridging formate plane and O–Mn–O axis respectively make angles of 76.1 (4) and 87.63 (4)° with the terminal porphyrin plane, and 77.6 (4) and 84.58 (2)° with the central porphyrin plane. Phenyl residue contact in **2** is minimized by a rotation of the central porphyrin ligand about the trimer axis by 31.4° and a tilting of the two crystallographically independent ligands to form angles of 68.73 (4) and 68.98 (4)° with the trimer axis. The dihedral angle formed by these two planes is 39.57 (5)°. The central porphyrin skeleton is essentially planar with the largest non-hydrogen displacement being 0.084 (8) Å. The terminal porphyrin ligand has a ruf[31] core conformation and the largest displacement from the 24-atom least-squares plane is 0.460 Å. The manganese ion is displaced by 0.048 (1) Å from the 24-atom plane and 0.039 (1) Å from the nitrogen core, and the distance between this ion and the central metal ion is 6.337 Å.

Complex **2** can be regarded as a fragment of a "fractured polymer" in which adjacent trimeric components of the "ruptured chain" have a longitudinal separation of 1.104 Å and a transverse displacement of 4.241 Å to give an overall distance of 8.565 Å between terminal Mn sites. The distance between a terminal Mn site and the uncoordinated oxygen site of a terminal formate ligand on an adjacent fragment is 4.526 Å. It is not clear whether the failure to form a polymer is associated with the chloroform solvate or the rapidity with which the crystals were obtained (perhaps both). The direction and packing of the chain fragments of the trimeric complex **2** is quite different to that of the chains in the polymeric complex **1**. The unit cell of **2** is partially penetrated by two trimers (fragments of adjacent fractured chains) on either side of the (110) plane, with the Mn–Mn–Mn trimer axes being approximately aligned with the line between the points (1, 0, 0.5) and (0, 1, 0.5) on the (110) plane. Unit cells stacked in the *a* and *b* directions form layers of "fractured", chains and these layers are stacked in the *c* direction. The distance between the principal axes of the two trimers partially penetrating the unit cell is 11.512 Å and is effectively the distance between adjacent pseudo chains within a layer. The distance between the layers stacked in the *c* direction is 12.862 Å. The shortest distance between the two trimers penetrating a unit cell is 3.615 Å between a phenyl meta carbon site and a pyrrole β-carbon site. The shortest distance between locations on trimers stacked in the *c* direction is 3.410 Å between a phenyl meta carbon site and an phenyl ortho carbon site. There are three crystallographically unique chloroform sites in cavities formed between the porphyrin planes of neighboring trimers. All three solvent sites exhibit very high thermal motion, and our attempts to account for the high temperature factors with a disordered solvent model were unsuccessful. The most stable solvent site is bounded by the terminal and central ligands of one trimer and a terminal ligand of a neighboring trimer. The other two solvent sites are less contrained and are located between the terminal planes of two fragments of the same ruptured chain.

As part of a general investigation of the solution and solid-state properties of manganese tetraphenylporphyrin complexes,[27] we have solved the structures of the potentially polymeric complexes $(TPP)Mn(CH_3CO_2)$, (TPP)Mn(OCN), and (TPP)Mn(SCN) and found them to be monomeric[32] (grown from toluene–heptane mixtures). However, Armstrong, Foran, and Hambley[33] have recently obtained a polymeric $[(TPP)Mn(CH_3CO_2)]_n$ complex from THF. The only other manganese porphyrin polymer complex reported to date,[9] $[(TPP)Mn(imidazolate)]_n$, has an imidazolate bridging ligand that induces alternating long and short $Mn–N_{Im}$ bond lengths that reflect alternating low and high spin states in the metal ions of the polymer chain. Alternating bond lengths are not found in the formato polymer, and it is likely, therefore, that the metal ion spin state is constant across the polymer chain. A detailed magnetic characterization is expected to be completed in the near future. The bridging formate ligand offers an effective superexchange pathway, better than the acetate ion for instance.[34] Given that the formate ligand may well be a better π-donor than a σ-donor in manganese tetraphenylporphyrin complexes,[27] an antiferromagnetic exchange interaction can be anticipated for the anti–anti-bridged[35] complexes **1** and **2**. Work on the formato complexes continues, and we are further attempting to define the general requirements for the axial polymerization of manganese tetraphenylporphyrin complexes.

Acknowledgment. This research was supported by the Australian Research Council.

Supplementary Material Available: For complex **1** a figure showing the carbonyl region of the IR spectrum, a diagram showing the atom numbering, and listings of positional parameters, bond lengths, bond angles, thermal parameters, hydrogen atom positional and thermal parameters, and least-squares planes and for complex **2** diagrams showing the atom numbering and listings of bond lengths, bond angles, non-hydrogen positional parameters, anisotropic displacement parameters, hydrogen atom positional and isotropic parameters, least-squares planes, and dihedral angles (43 pages); listings of observed and calculated structure factors for both complexes (59 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of New England
Armidale, NSW 2351, Australia
Peter Turner*
Maxwell J. Gunter

School of Chemistry
University of Sydney
Sydney, NSW 2006, Australia
Trevor W. Hambley

Department of Chemistry
University of Western Australia
Perth, WA 6009, Australia
Allan H. White
Brian W. Skelton

Received December 4, 1991

---

(30) $[(TPP)Mn(HCO_2)]_3(H_2O)\cdot 6CHCl_3$, $C_{135}H_{89}N_{12}Mn_3O_7\cdot 6CHCl_3$: $M = 2872.20$; very dark green, triclinic, space group $P\bar{1}$, $a = 17.994$ (6) Å, $b = 14.22$ (3) Å, $c = 13.205$ (7) Å, $\alpha = 85.87$ (9)°, $\beta = 82.88$ (4)°, $\gamma = 78.35$ (9)°, $Z = 1$, $V = 3280$ (7) Å^3, $D_c = 1.44$ g cm^{-3}, $T = 295$ K; crystal dimensions 0.3 × 0.6 × 0.4 mm, μ(Mo, $K\alpha$) = 6.35 cm^{-1}, A^*(min,max) = 1.235, 1.343 (analytical correction); Enraf-Nonius CAD-4 diffractometer, λ(Mo Kα, graphite monochrometer) = 0.7107 Å, N(θ_{max} = 25°; ω/θ mode) = 11 514, $N_0(I > 3\sigma(I)) = 6887$, number of variables = 831, $F_{000} = 1462$; Range of *hkl* ±21, ±16, 0 to 15; $R = 0.083$, $R_w = 0.090$; Heavy atom solution with XTAL 3.0 program suite (Hall, S. R.; Stewart, J. M., Eds. *Xtal 3.0 Reference Manual*; Universities of Western Australia and Maryland, 1990). Anisotropic thermal parameters were refined for the non-hydrogen atoms and (x, y, z, U_{iso}) for hydrogen atoms were constrained at estimated values; neutral atom scattering factors were utilized; there was no extinction. High residuals appear to be primarily a consequence of very high thermal motion of the solvent, possibly a foil for disorder and partial site occupancy. Refinement of the latter gave values of 0.987 (3), 0.959 (4), and 0.905 (4) for the independent solvent molecules. Attempts to account for the thermal motion with a disorder model proved fruitless.

(31) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding* **1987**, *64*, 1.

(32) Turner, P.; Gunter, M. J.; Skelton, B. W.; White, A. H. Manuscript in preparation.

(33) Armstrong, R. S.; Foran, G. A.; Hambley, T. W. Private communication.

(34) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209.

(35) Inoue, M.; Kubo, M. *Inorg. Chem.* **1970**, *9*, 2310.

Examples of Large Closo Boron Hydride Analogs of Carbon Fullerenes

There exists a geometrical correspondence between the large closo boron hydrides and their analog carbon fullerenes. Thus, the aromatic molecule $B_{32}H_{32}$, of icosahedral symmetry, the structure of which has been proposed some time ago[1] is the analog

---

(1) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 3443.

0020-1669/92/1331-2297$03.00/0 © 1992 American Chemical Society