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.

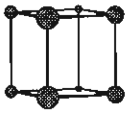
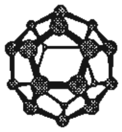
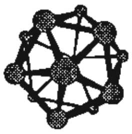
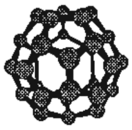
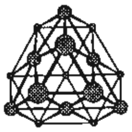
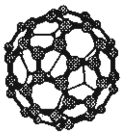
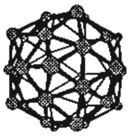
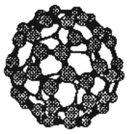
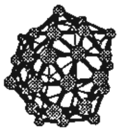
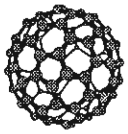
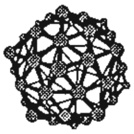
Examples of Large Closo Boron Hydride Analogs of Carbon Fullerenes

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.

Table I. Carbon Compounds and Their Boron Analogs

diagram	molecule	*P*	*F*	*C* + 2	sym	*P*	*F*	molecule[a]	diagram
	C_4	4	4	8	T_d	4	4	B_4H_4	
	C_8	8	6	14	O_h	6	8	B_6H_6	
	C_{20}	20	12	32	I_h	12	20	$B_{12}H_{12}$	
	C_{28}	28	16	44	T_d	16	28	$B_{16}H_{16}$	
	C_{60}	60	32	92	I_h	32	60	$B_{32}H_{32}$	
	C_{70}	70	37	107	D_{5h}	37	70	$B_{37}H_{37}$	
	C_{80}	80	42	122	I_h	42	80	$B_{42}H_{42}$	

[a] B_4H_4 is predicted to be neutral, B_6H_6 and $B_{12}H_{12}$ are −2 ions, and probable charges of the larger boron species are yet to be examined using MO methods.

of the Buckminster fullerene molecule C_{60}. The correspondence referred to is based upon the following: (a) symmetry; (b) number equality of (i) carbon faces and boron vertices, (ii) boron faces and carbon vertices, and (iii) carbon contacts and boron contacts; (c) sphericity.

The correspondence is illuminated by application of the Descartes–Euler formula[2]

$$P + F = C + 2 \qquad (1)$$

to both sets of polyhedra to relate within one molecule the number of vertices, *P*, the number of faces, *F*, and the number of contacts, *C*.

In Table I we list a few examples of the geometrical correspondence which prevails between closo boron hydrides and the carbon fullerenes. In particular, one may note how the geometrical structure of Buckminster fullerene maps into that of the 32 vertex closo boron hydride, $B_{32}H_{32}$. Both molecules of symmetry I_h display correspondence of the geometrical centers of the 32 carbon (polygon) faces to the 32 boron vertices, the 60 boron faces to the 60 carbon vertices, and the 90 carbon contacts to the 90 boron contacts. The sphericity[3] of each compound is maximal within its class. In accordance with eq 1, for both molecules the sum of the vertices and faces exceeds by 2 the number of contacts. A cursory review of Table I indicates that similar correspondences prevail for all the examples listed. Clearly the list of examples may be readily extended.

We mention in passing that eq 1 may be used to predict quickly which closo boron hydride is the analog of each experimentally known fullerene. Thus, for a given fullerene, if the number of carbons is multiplied by $^3/_2$ (a formal carbon contact number) to give the total number of carbon contacts, one may then calculate the number of carbon faces whose equality with the number of boron vertices yields immediately the molecular formula desired.

In view of the successes achieved in producing macroscopic quantities of the fullerenes,[4] analogous methods might be used to synthesize their closo boron hydride analogs. For this purpose we suggest the possibility of laser ablation "graphitic" MB_2 (e.g. M = Ca^{2+}) in an atmosphere of H_2 to search for $B_{32}H_{32}$, which may or may not contain an internal charge-compensating metal ion.

As has occurred with the fullerenes,[5] it is reasonable to suppose a remarkable variety of molecular properties might be associated

---

(2) Coxeter, H. S. M. *Introduction to Geometry*; John Wiley & Sons: New York, 1961.

(3) A numerical measure of sphericity may be taken to be $S = 1 - [\langle R^2\rangle - \langle R\rangle^2]^{1/2}/\langle R\rangle$. This yields a limiting value for a sphere of (1.0) and for the five platonic solids the values (0.966), (0.924), (0.899), (0.828), and (0.723), respectively, for a dodecahedron, icosahedron, cube, octahedron, and tetrahedron. See also related discussion in ref 1.

(4) (a) Kratschmer, K.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) The fullerenes were made in lesser quantity earlier: Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (c) To the best knowledge of the authors, the earliest suggestion that C_{60} should be a stable, "spherical", superconjugated molecule was made by: Eiji Osawa; Osawa, E. *Chemistry* **1970**, *25* (9), 854 (in Japanese). Yoshida, Z.; Osawa, E. *Aromaticity*; Kagakudojin: Kyoto, Japan 1971; pp 174–178 (in Japanese).

(5) Koshland, D. E., Jr. *Science* **1991**, *254*, 1705.

with the large closo boron hydrides, which are their geometrical duals.[6]

Acknowledgment. We thank M. Gee for model building, J. Wolff of Cambridge Scientific Computing, L. Huang and S. Chen for computer drawing, and R. C. Stevens for discussions.

---

(6) Coxeter, H. S. M. *Regular Polytopes*; Dover: New York, 1973. Note: Dual polyhedra are also known as reciprocals.

(7) Visiting Scholar, Hunter College and the Graduate School, City University of New York, New York, NY 10021.

Gibbs Chemical Laboratory
Harvard University
Cambridge, Massachusetts 02138

William N. Lipscomb*
Lou Massa[7]

Received March 25, 1992

Stereochemistry of Six-Coordinated Silicon Complexes. 2. Optical Resolution of $[Si(\alpha\text{-diimine})_3]^{4+}$ (α-Diimine = bpy, phen)

Six-coordinated complexes of silicon(IV) are not very familiar as compared to four-coordinated tetrahedral compounds. Though several six-coordinated Si(IV) complexes have already been synthesized, there are few studies of the isomerism.

In the present paper, we report the complete optical resolution of $[Si(phen)_3]^{4+}$. $[Si(phen)_3]^{4+}$ was synthesized from SiI_4 and 1,10-phenanthroline following the literature method[1] and chromatographically purified. The resolution was performed by a chromatographic method using an SP-Sephadex C-25 column (ϕ = 1.1 cm × 46 cm) as an adsorbent and a 0.08 M aqueous solution of sodium ((+)-tartrato)antimonate(III),[2] $Na_2[Sb_2\{(+)\text{-tart}\}_2]$ as an eluent. Figure 1 shows the elution curve. The two elution bands are completely separated, and complete resolution is effectively achieved. Each enantiomer is so stable in aqueous solution that the absorption spectrum and optical rotation were unchanged after a month at room temperature. There are some examples of enantiomeric six-coordinated silicon(IV) complexes,[3-6] but all of them are unstable in aqueous solutions. This is the first example of stable (in water) enantiomers of six-coordinated octahedral silicon(IV) complexes. The absorption and circular dichroism (CD) spectra are shown in Figure 2. According to exciton theory,[7] the absolute configuration of the faster-moving $(+)_{589}$ isomer can be assigned to Λ. Though we have already attempted the resolution of $[Si(bpy)_3]^{4+}$ by a chromatographic method, the separation of enantiomers was insufficient under the same conditions. Sodium (+)-tartrate was found to be a less effective eluting agent for both complexes.

The elution order (Λ moves faster than Δ) of the enantiomers for both the bpy and phen complexes is the same as that observed for the corresponding cobalt(III) complexes.[2]

The ^1H NMR spectra of $[Si(bpy)_3]^{4+}$ and $[Si(phen)_3]^{4+}$ were measured in the presence and absence of $[Sb_2\{(+)\text{-tart}\}_2]^{2-}$, in order to elucidate the mechanism of the chromatographic resolution, i.e. the stereoselective interaction between the complex ions and (tartrato)antimonate(III) ions. Figures 3 and 4 show the ^1H NMR spectra of an ca. 0.02 M D_2O solution of $[Si(bpy)_3]^{4+}$ and an ca. 0.004 M D_2O solution of $[Si(phen)_3]^{4+}$, respectively. The largest

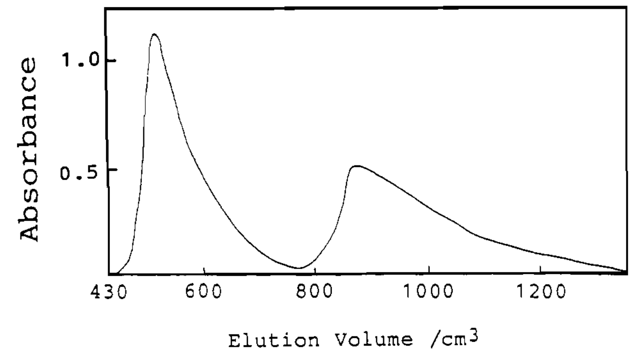


Figure 1. Elution curve of $[Si(phen)_3]^{4+}$ on an SP-Sephadex column. Chromatographic conditions: column, SP-Sephadex C-25, ϕ = 1.1 cm × 46 cm; eluent, $Na_2[Sb_2\{(+)\text{-tart}\}_2]$ (0.08 M); flow rate, 0.8 cm³ min⁻¹; UV detection, 290 nm.

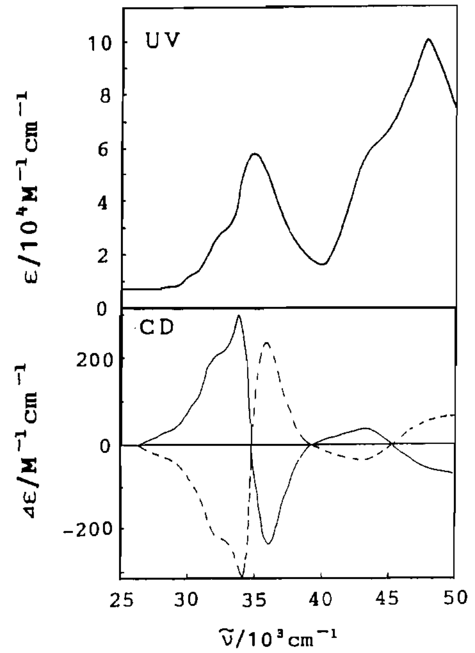


Figure 2. Absorption and CD spectra of $(+)_{589}$ (Λ)- (—) and $(-)_{589}$ (Δ)-$[Si(phen)_3]^{4+}$ (– –).

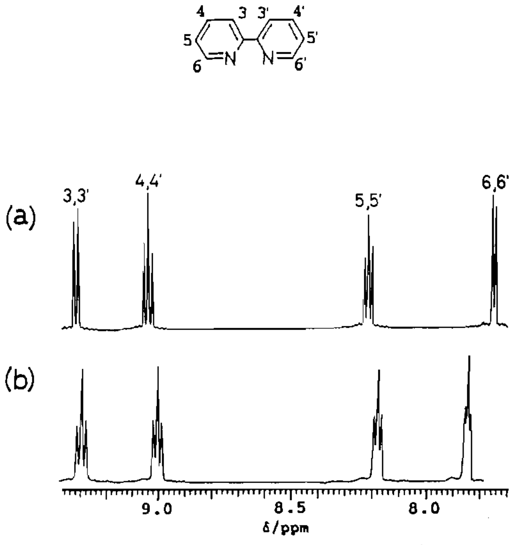


Figure 3. ^1H NMR spectra (500 MHz) of $[Si(bpy)_3]^{4+}$ (ca. 0.02 M) in D_2O, (a) in the absence and (b) in the presence of $Na_2[Sb_2\{(+)\text{-tart}\}_2]$ (0.4 M).

---

(1) Kummer, D.; Gaisser, K. E.; Seifert, J.; Wagner, R. *Z. Anorg. Allg. Chem.* **1979**, *459*, 145.

(2) Yoshikawa, Y.; Yamasaki, K. *Coord. Chem. Rev.* **1979**, *28*, 205.

(3) Dhar, S. K.; Dorn, V.; Kirschner, S. *J. Am. Chem. Soc.* **1958**, *80*, 753.

(4) Larsen, E.; Mason, S. F.; Searle, G. H. *Acta Chem. Scand.* **1966**, *20*, 191.

(5) Inoue, T.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1228.

(6) Inoue, T. *Inorg. Chem.* **1983**, *22*, 2435.

(7) (a) Mason, S. F.; Norman, B. J. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 285. (b) Mason, S. F. *Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism*; Heyden & Son: Philadelphia, PA, 1973; pp 196–239.

0020-1669/92/1331-2299$03.00/0