Novel Metalloporphyrins—Syntheses and Implications

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The last few years have seen substantial growth in metalloporphyrin research. Certainly most of this stems from interest in the biological systems to which these compounds are related. However metalloporphyrins are also studied for other reasons. These include the search for new semiconductors,[1] superconductors,[2] anticancer drugs,[3] and catalysts.[4] Several porphyrin-related compounds, particularly the phthalocyanines,[5] have proved useful as dyes. Even without their biological and industrial implications the properties of metalloporphyrins would be studied for their purely theoretical importance. Thus, even to the nonspecialist, a knowledge of the more recent or unusual synthetic metalloporphyrins could be useful.

The porphyrins are compounds formed by adding substituents to the nucleus of porphine (1). The nat-


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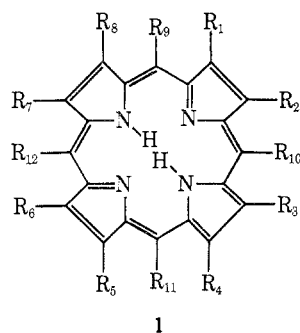
urally occurring porphyrins are generally formed by adding substituents to positions 1-8 and are named according to the number and type of substituents. The roman numerals after the name indicate the pattern of substitution. Of the large number of possible arrangements, few have been found in nature. Table I lists several porphyrins, both natural and synthetic, along with their trivial names. Certain common porphyrins will hereafter be referred to by abbreviations listed in Table I.

Upon removal of the pyrrole protons, porphyrins readily complex with a variety of metals. While free

porphyrins are biologically unimportant, metalloporphyrins are widely found in nature. It is with certain of these metal complexes that this Account deals.
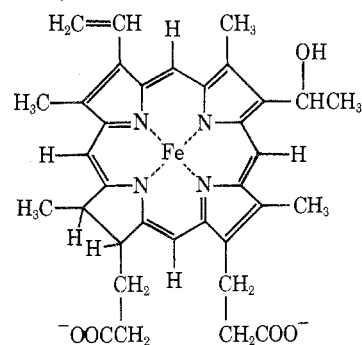
Several biologically important porphyrin-containing species are listed in Table II. Strictly speaking, chlorophyll, cobalamin, and the *d* cytochromes are not porphyrins (2-4), but the similarity between
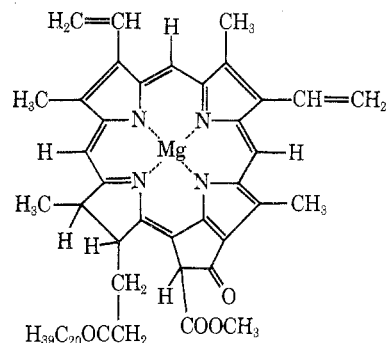
2, tetrapyrrole complex from chlorophyll a
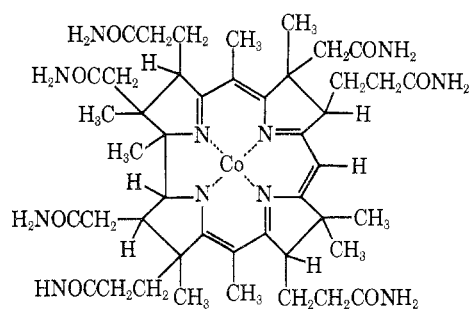
3, tetrapyrrole complex from cobalamin

4, tetrapyrrole complex from cytochrome *d*

David Ostfeld was born in Chicago in 1942. He earned his B.S. in Chemistry from the University of Illinois and his Ph.D. from Cornell University. Three years of postdoctoral work, including a year with Professor Tsutsui, were devoted to studying metalloporphyrin chemistry. Currently he is Assistant Professor of Chemistry at Seton Hall University.

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(2) A. D. Adler, *J. Polym. Sci., Part C*, 29, 73 (1970).
(3) J. P. Macquet and T. Theophanides, *Can. J. Chem.*, 51, 219 (1972).
(4) E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, 94, 1382 (1972).
(5) D. Patterson, "Pigments, an Introduction to Their Physical Chemistry," Elsevier, New York, N. Y., 1967, p 44.

Table I
Some Common Porphyrins and Their Trivial Names

Porphyrin	Position on ring[a]								
	1	2	3	4	5	6	7	8	9–12
Proto-porphyrin IX	M	V	M	V	M	P	P	M	H
Deutero-porphyrin IX	M	H	M	H	M	P	P	M	H
Hemato-porphyrin IX	M	B	M	B	M	P	P	M	H
Meso-porphyrin IX[b]	M	E	M	E	M	P	P	M	H
Phylloporphyrin	M	E	M	E	M	H	P	M	CH₃ + 3 H
Tetraphenyl-porphine[c]	H	H	H	H	H	H	H	H	C₆H₅
Octaethyl-porphine[d]	E	E	E	E	E	E	E	E	H

[a] A, CH_2COOH; B, $CHOHCH_3$; E, CH_2CH_3; M, CH_3; P, CH_2CH_2COOH; V, $CHCH_2$. [b] H_2MP. [c] H_2TPP. [d] H_2OEP.

these heterocycles and the porphyrins is obvious. Biosynthesis of certain chlorophylls is even known to involve magnesium protoporphyrin as an intermediate.[6] It is therefore generally acceptable to consider model studies on porphyrins as applicable to cobalamin, the chlorophylls, and other nonporphyrin macrocycles.

The study of porphyrin chemistry can be said[7] to have begun in 1880 with Hoppe-Seyler's isolation of hematoporphyrin from hemin (5) and phylloporphy-
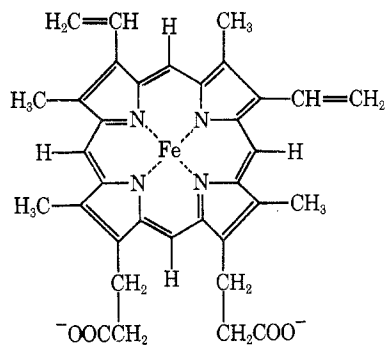
5, tetrapyrrole complex from hemoglobin

rin from chlorophyll (2). In isolating the dematalated macrocycles, he showed the similarity that existed between these two molecules.

In 1902 the first "novel metalloporphyrins," meso-porphyrin IX complexes of Cu(II) and Zn(II), were prepared.[8] This was actually 2 years before the first successful reinsertion of iron into a demetalated porphyrin.[9] From studies of these compounds it was found that mesoporphyrin complexes of zinc and copper, metals lacking a common 3+ state, contain no chlorine. This showed the chlorine in [porphyrin-iron(III) chloride] to be bound to the metal and not to the porphyrin.

Synthetic work continued so that, by 1964, Falk[10] was able to list porphyrin complexes for 28 metallic

Table II
Some Biological Compounds Containing Porphyrin-like Ligands

Compound	Metal	Compound	Metal
Hemoglobin	Fe	Peroxidase	Fe
Myoglobin	Fe	Oxidase	Fe
Cytochrome	Fe	Cobalamin (vitamin B₁₂)	Co
Catalase	Fe	Chlorophyll	Mg

elements. Figure 1 contrasts the metals for which porphyrin complexes were listed by Falk with those for which such complexes have subsequently been prepared. References are given to the syntheses of the new compounds.[11-30]

The characteristics which porphyrins share with other multidentate nitrogen-donor ligands need not be discussed here. What must be emphasized are those characteristics unique to the porphyrin ligand.

Porphyrins, in common with other macrocyclic ligands, have a central hole of essentially fixed size. In certain complexes the metal is unable to fit into this hole and, as has been shown by Hoard,[31] lies out of the porphyrin plane. In hemoglobin, for example, the iron atom in the oxygenated form lies roughly in plane, while the metal lies out of plane in the deoxy form. The transition between these states is thought to be responsible for the cooperative nature of oxygen binding in hemoglobin.[32]

Also characteristic of complexes of porphyrins and other macrocycles is the necessity of simultaneously breaking all metal–ligand bonds to remove the ligand. Using several macrocyclic ligands, Busch and coworkers demonstrated[33] that, consequently, the

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(25) Z. Yoshida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Lett.*, 1077 (1972).

(26) H. Ogoshi, T. Omura, and Z. Yoshida, *J. Amer. Chem. Soc.*, **95**, 1668 (1973).

(27) B. R. James and D. V. Stynes, *J. Amer. Chem. Soc.*, **94**, 6225 (1972).

(28) D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Amer. Chem. Soc.*, **93**, 2548 (1971).

(29) E. B. Fleischer and A. Laszlo, *Inorg. Nucl. Chem. Lett.*, **5**, 373 (1969).

(30) M. Tsutsui and C. P. Hrung, *Chem. Lett.*, 941 (1973).

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Figure 1. Metals for which porphyrin complexes have been made: □, porphyrins mentioned by Falk;[10] ▫, more recent metalloporphyrins.

dissociation of a metal–macrocycle complex is about 10^6 times slower than for a similar noncyclic ligand.

Porphyrins and certain other unsaturated ligands (*e.g.*, bipyridyl) are distinguished by their delocalized π systems. Overlap between ligand π orbitals and metal orbitals of proper symmetry produces a moderately high ligand field strength.[34] Also, by back-accepting π electron density from complexed metals, the ligands facilitate the reduction of complexed metal to a low oxidation state.[27,35,36] It should be mentioned, however, that not all unusual porphyrin oxidation states are so easily explained. For example, the most stable silver porphyrin has the metal in a 2+ and not a 1+ state.[37] No explanation for this has yet been proposed.

Synthesis

The first of the new synthetic methods to be discovered was the insertion of a metal from a carbonyl complex.[17,38] Instead of simple ligand exchange with the porphyrin dianion, the porphyrin is oxidized by the reduction of the porphyrin pyrrole protons. For example, letting Por stand for porphyrin

$$Cr(CO)_6 \ + \ PorH_2 \ \xrightarrow[\text{decalin}]{185°} \ [Por-Cr^{II}] \ + \ 6CO\uparrow \ + \ H_2\uparrow$$
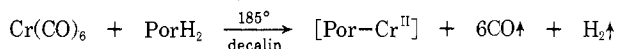
The mechanism for this class of reaction has never been studied, but it is assumed that the evolution of hydrogen and carbon monoxide drives the equilibrium toward metal insertion. By inference from the rhenium complexes (discussed later) it can be surmised that the metal is oxidized in a series of one-electron steps, each of which is accompanied by the reduction of a pyrrole proton.

$$M(0) \ + \ PorH_2 \ \longrightarrow \ [HPor-M^I] \ + \ H_2\uparrow$$

$$[HPor-M^I] \ \longrightarrow \ [Por-M^{II}] \ + \ H_2\uparrow$$
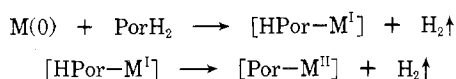
The carbonyl method has been used to synthesize previously unknown complexes of chromium,[17,38] molybdenum,[20] ruthenium,[21,22] rhodium,[23] iridium,[23] rhenium,[28] and technetium.[30] Metalloporphy-

rins containing some of these metals [chromium,[14,15] molybdenum,[15] rhodium,[39] and rhenium[19]] have subsequently been prepared by other methods, but the complexes formed from carbonyls are still unique. In some cases [ruthenium(II), iridium(I), rhenium(I), and technetium(I)] a carbonyl ligand is retained by the metal. Also low oxidation states are generally obtained from metal carbonyls. Several novel metal(I) porphyrin complexes which have been prepared using metal carbonyls (discussed later) are certainly unique to this method.
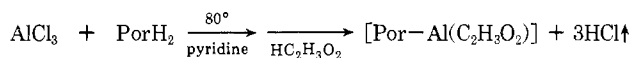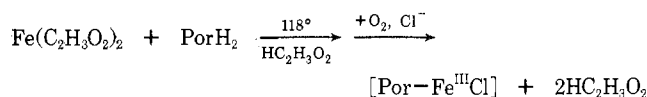
A similar method involves the oxidation of hydride ions from a metal hydride complex. For example[40]

$$AlH_3 \ + \ PorH_2 \ \xrightarrow[\text{THF}]{65° \quad +H_2O} \ [Por-AlOH] \ + \ 3H_2\uparrow$$
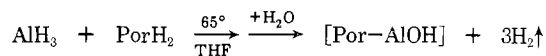
The small number of metals for which hydrides are available has probably restricted the use of this method. One other example of a metal hydride reacting with a porphyrin is the reaction of sodium borohydride with tetraphenylporphine. The product, which has never been characterized, may be a boron porphyrin.[41]

It does not appear that the utility of these reactions is enhanced by the oxidation and reduction. A more likely explanation for their success is that: (1) the evolution of gas drives the reaction to completion; (2) metal carbonyls and hydrides dissolve in the same organic solvents as do the porphyrins.

Previously the porphyrin and the metal salt had been dissolved by using an acidic or basic medium (*e.g.*, acetic acid[42] or pyridine[12]). As was pointed out

$$Fe(C_2H_3O_2)_2 \ + \ PorH_2 \ \xrightarrow[\text{HC}_2\text{H}_3\text{O}_2]{118° \quad +O_2, \ Cl^-}$$

$$[Por-Fe^{III}Cl] \ + \ 2HC_2H_3O_2$$

$$AlCl_3 \ + \ PorH_2 \ \xrightarrow[\text{pyridine} \quad \text{HC}_2\text{H}_3\text{O}_2]{80°} \ [Por-Al(C_2H_3O_2)] \ + \ 3HCl\uparrow$$

by Adler,[14] these reactions have some serious flaws. In an acidic medium the porphyrin exists primarily in the unreactive protonated form; in basic media the reactivity of the metal is decreased by complexation with hydroxide, pyridine, etc.

The solubility problem was circumvented by Tsutsui through the use of an organometallic compound

(34) Good discussions of the electronic structure of metalloporphyrins are given by: M. Zerner, M. Gouterman, and H. Kobayashi, *Theoret. Chem. Acta*, **6**, 363 (1966); H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jap.*, **45**, 450 (1972).

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(39) L. K. Hanson, M. Gouterman, and J. C. Hanson, *J. Amer. Chem. Soc.*, **95**, 4822 (1973).

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(42) D. W. Thomas and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 5111 (1959).

as a metal source. Diphenyltitanium was found to react with mesoporphyrin IX dimethyl ester to give the titanyl porphyrin.[16] The organometallic com-

$$(C_6H_5)_2Ti + PorH_2 \xrightarrow[mentylene]{240°} \xrightarrow{+O_2} [Por-Ti=O] + 2C_6H_6$$
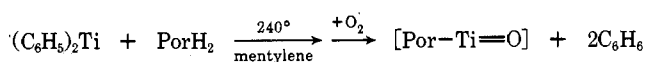
pound used here is soluble in nonpolar organic solvents, and the stable organic moiety formed in the reaction helps drive the equilibrium in the desired direction. Presumably air oxidizes the titanium to the 4+ state. Other organometallics could be used in a similar manner. Indeed, the use of organometallics is probably one of the most powerful methods available for metal insertion. However, the inconvenience involved in choosing and obtaining organometallic derivatives and the availability of other methods have prevented greater use of organometallics as starting materials.

Buchler and coworkers[15] found metal acetylacetonates both readily available and reasonably soluble in organic solvents. They studied the reaction of octaethylporphine with a number of metal acetylacetonates, using melts of phenol, quinoline, and imidazole as solvents.

$$M(acac)_n + PorH_2 \longrightarrow [Por-M(acac)_{n-2}] + 2Hacac$$
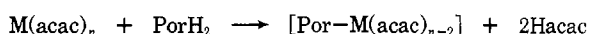
Besides a number of previously known metalloporphyrins, new complexes of scandium and zirconium were prepared. Of their reactions the only ones that failed were attempted syntheses of cerium and thorium porphyrins.

Instead of supplying the metal in the form of a complex, Adler and coworkers solved the solubility problem by using N,N-dimethylformamide (DMF) as a solvent.[14] DMF, due to its high dielectric constant, can dissolve both a porphyrin and a metal salt. While one cannot exclude the possibility of another form of solvent assistance, such as a stabilized transition state, no evidence of this has been found. Adler obtained improved yields of many known compounds by using DMF. This method may also be useful for the synthesis of new compounds. Among the compounds thus synthesized was the once-elusive chromium porphyrin. Due to the simplicity of

$$4PorH_2 + 4CrCl_2 + O_2 \xrightarrow[DMF]{153°}$$
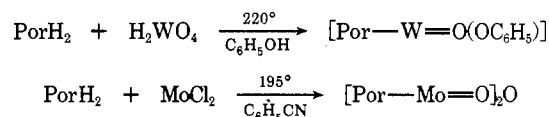$$4[Por-Cr^{III}Cl] + 4HCl\uparrow + 2H_2O$$
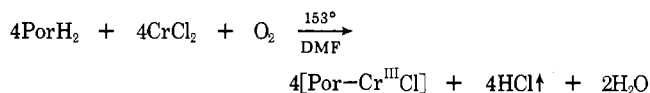
this method and the ready availability of starting materials, it is not surprising to see compounds which were once made by other methods now being prepared in DMF.[39]

The use of polar reaction media had not been previously unknown. It is presumably due to their lower dielectric constants that solvents such as acetone, dioxane, and ethanol[43] were not so successful as DMF.

Buchler[18] further extended the synthesis of metalloporphyrins in media of high dielectric constant. Using a phenol melt and appropriate metal halides or oxides, he prepared complexes of scandium, tantalum, tungsten, osmium, and rhenium. In benzonitrile, porphyrins and metal halides reacted to give an equally novel array of metalloporphyrins, including

those of chromium, molybdenum, tungsten, and niobium. For example

$$PorH_2 + H_2WO_4 \xrightarrow[C_6H_5OH]{220°} [Por-W=O(OC_6H_5)]$$

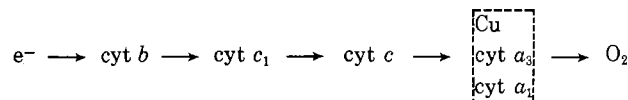$$PorH_2 + MoCl_2 \xrightarrow[C_6H_5CN]{195°} [Por-Mo=O]_2O$$

A tungsten complex is particularly noteworthy, since attempted syntheses using tungsten hexacarbonyl had been unsuccessful.[44]

Except for the lanthanides and actinides, at least one porphyrin complex has been made for virtually every metallic element. However, due to the importance of oxidation state and axial ligation it would be incorrect to assume that all porphyrin complexes of potential interest are known. What might be stated is that any reasonable porphyrin complex desired by the modern chemist should be attainable through the powerful synthetic methods now available.

Bridged and Metal–Metal-Bonded Species

Among the reasons for interest in bridged and metal–metal-bonded complexes has been the desire to prepare model compounds for studying the role of heme iron in mitochondrial electron transfer.[45] In mitochondria, the cellular bodies in which oxidation occurs, heme proteins called cytochromes are crucial links in the electron-transfer chain. A typical chain, as found in beef heart, is[46]

$$e^- \longrightarrow cyt\ b \longrightarrow cyt\ c_1 \longrightarrow cyt\ c \longrightarrow \begin{bmatrix} Cu \\ cyt\ a_3 \\ cyt\ a \end{bmatrix} \longrightarrow O_2$$

The classes of cytochromes (a, b, c, etc.) differ in their spectra, oxidation potentials, porphyrin substitution patterns, and attached proteins. However all (except the d cytochromes) are iron porphyrins.

While electron transfer via the porphyrin ring is a possibility,[47] work has concentrated on transfer through the axial sites.[48] Cytochrome b is known to coordinate two imidazoles in its axial position,[49] while the c cytochromes bind to an imidazole and a methionine sulfur.[50] It has been theorized that an electron leaving cytochrome c goes by way of the methionine sulfur.[51] Imidazole, with its double bonds, could also be a suitable bridge for electron transfer.

Ostfeld and Cohen[52] have studied the polymer [-(FeTPP)-(imidazolate)-]$_n$ (6). Magnetic studies indicate spin coupling through the imidazolate ligands, thus demonstrating the ability of this ligand to serve as an electron bridge when complexed to an iron porphyrin.

(44) T. S. Srivastava and M. Tsutsui, unpublished observations.
(45) W. S. Caughey, J. L. Davies, W. H. Fuchsman, and S. McCoy in "Structure and Function of Cytochromes," K. Okunuki, M. D. Kamen, and I. Sekuzu, Ed., University Park Press, Baltimore, Md., 1968, p 20.
(46) H. R. Mahler and E. H. Cordes, "Biological Chemistry," Harper and Row, New York, N. Y., 1971, p 683.
(47) C. E. Castro and H. F. Davis, *J. Amer. Chem. Soc.*, 91, 5405 (1969).
(48) I. A. Cohen, C. Jung, and T. Governo, *J. Amer. Chem. Soc.*, 94, 3003 (1972).
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(50) R. E. Dickerson, T. Takano, D. Eisenberg, O. B. Kallai, L. Samson, A. Cooper, and E. Margoliash, *J. Biol. Chem.*, 246, 1511 (1971).
(51) T. Takano, R. Swanson, O. B. Kallai, and R. E. Dickerson, *Cold Stream Harbor Symp. Quant. Biol.*, 36, 397 (1971).
(52) D. Ostfeld and I. A. Cohen, submitted for publication.
(43) Reference 5, p 135.

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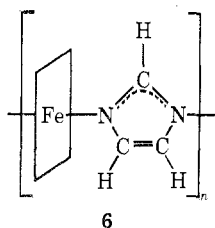
Compared to the *b* and *c* cytochromes, considerably less is known about the structure of cytochrome oxidase (the boxed species in the electron-transfer scheme shown above). Even the order of and connection between the copper and the *a* cytochromes are unclear. For this reason a variety of model compounds can be considered relevant to the cytochrome oxidase system.[53]

The best known example of metal–metal interaction in metalloporphyrins is the oxo-bridged "hematin" dimer **7**, only recently recognized to be a dimer and not a monomeric hydroxide.[54] The strong antiferromagnetic coupling[55] between the two iron(III) atoms shows the ability of this bridge to conduct electrons. Caughey[53] has proposed the possibility of iron–iron or iron–copper oxo bridges in cytochrome oxidase. Similar oxygen-bridged dimers have also been prepared for porphyrins of aluminum(III)[40] and scandium(III).[15] In porphyrin complexes of niobium, molybdenum, tungsten, and rhenium, two O=M(V) groups are joined by an oxygen bridge (**8**).[19]

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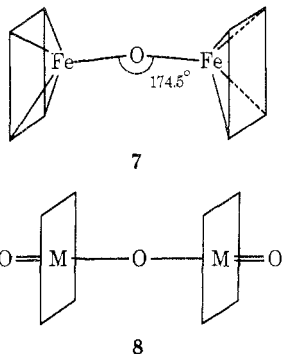
Like the iron dimer, the scandium dimer forms instead of the nonexistent monomeric hydroxide.[15] The porphyrin hydroxide of aluminum(III), however, does exist and is dimerized by heating under vacuum.[40] This leads to the possibility that other 3+

$$[\text{Por}-\text{Al}^{III}(\text{OH})] \xrightarrow[\text{vacuum}]{\Delta} [\text{Por}-\text{Al}^{III}-\text{O}-\text{Al}^{III}-\text{Por}]$$
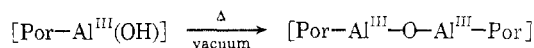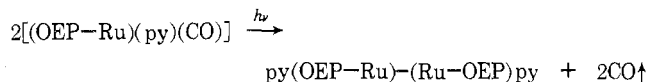
metals [*e.g.*, Co(III), Mn(III), Ga(III)] can form oxo-bridged porphyrin dimers upon removal of water from the hydroxide. An oxo-bridged dimer of manganese(III) phthalocyanine is, in fact, already known.[56]

Another recently prepared bridging system is a trimer involving two iron(III) porphyrin azides and an iron(II) porphyrin.[57] The magnetic moment of the ferric iron in this compound is 5.0 μ_B independent of temperature. This indicates the presence of four unpaired electrons instead of the five expected for high-

spin iron(III). That pairing occurs between only two of the electrons can be explained by the occurrence of a single orbital available for electron occupancy across the length of the molecule.

A good case for metal–metal bonding has been made by Whitten and coworkers[58] with the photochemical dimerization of ruthenium porphyrin. Upon irradiating a pyridine solution of ruthenium carbonyl octaethylporphine, two molecules of carbon monoxide are expelled.

$$2[(\text{OEP}-\text{Ru})(\text{py})(\text{CO})] \xrightarrow{h\nu}$$

$$\text{py}(\text{OEP}-\text{Ru})-(\text{Ru}-\text{OEP})\text{py} + 2\text{CO}\uparrow$$

This reaction does not occur when the porphyrin is tetraphenylporphine.[58] Presumably the TPP phenyl rings, which are known to lie almost perpendicular to the porphyrin plane,[59] interact such that two porphyrin molecules cannot approach sufficiently close for a metal–metal bond to form. Study of this compound by single-crystal X-ray diffraction would be desirable.

Metal–metal interaction also occurs in solid chromium(II) mesoporphyrin IX dimethyl ester. The magnetic moment of 2.84 μ_B[17] for each chromium atom is substantially less than the four-spin value of 4.90 μ_B expected[60] for square-planar chromium(II). However solutions of the chromium complex do not show a reduced moment, and a value of 5.19 μ_B is observed.[17] Apparently the close approach of chromium atoms in the solid phase causes a sufficient rise in the energy of the d_z orbitals to bring about electron pairing. As in the case of ruthenium porphyrin dimerization, tetraphenylporphine seems to inhibit metal–metal bonding. For solid Cr^{II}TPP a magnetic moment of 4.9 μ_B has been observed.[61] Metal–metal interaction may be a general phenomenon for paramagnetic metalloporphyrins containing no axial ligands, since a somewhat low magnetic moment has also been found for Rh^{II}TPP.[27]

The only known metal–metal bond in which a metalloporphyrin bonds to a nonporphyrin metal is an adduct of trimethyltin and iron tetraphenylporphine.[62] Mössbauer and far-ir data indicate that this air-sensitive, diamagnetic compound contains a metal–metal bond between iron(III) and tin(IV).

Unusual Geometries

Recent synthetic work can be used to show the geometric limits within which metalloporphyrin formation is possible. For example, the absence of porphyrin complexes for the lanthanide and actinide elements seems to indicate that metals above a certain size cannot be incorporated into a porphyrin ring. This is consistent with Hoard's finding[31] that iron in certain electronic states will not fit into a metalloporphyrin, but instead sits slightly out of the porphyrin plane.

Additional geometries which metalloporphyrins can assume are illustrated by two rhenium porphy-

(53) W. S. Caughey, *Advan. Chem. Ser.*, No. 100, 248 (1971).
(54) I. A. Cohen, *J. Amer. Chem. Soc.*, 91, 1980 (1969).
(55) T. H. Moss, H. R. Lilienthal, G. Moleski, G. A. Smythe, M. C. McDaniel, and W. S. Caughey, *J. Chem. Soc., Chem. Commun.*, 263 (1972).
(56) E. B. Fleischer, *Accounts Chem. Res.*, 3, 105 (1970).
(57) I. A. Cohen, *Ann. N. Y. Acad. Sci.*, 206, 453 (1973).

(58) W. Sovocol, F. R. Hopf, and D. G. Whitten, *J. Amer. Chem. Soc.*, 94, 4350 (1972).
(59) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, 86, 2342 (1964).
(60) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 134 (1964).
(61) N. J. Gogan and Z. U. Siddiqui, *Can. J. Chem.*, 50, 720 (1972).
(62) I. A. Cohen and B. Lichtenstein, to be published.

rins, μ-(Por)[Re(CO)$_3$]$_2$ and (PorH)Re(CO)$_3$.[28,63] The manner in which the metal atoms were bonded to the porphyrin ring was not initially clear, and several speculative structures were based[63] on the almost identical ir spectra given by the mono- and dirhenium complexes. A single-crystal X-ray diffraction analysis has given structure 9 for the dirhenium complex;[64] presumably the monorhenium complex is similar (10).

9

10
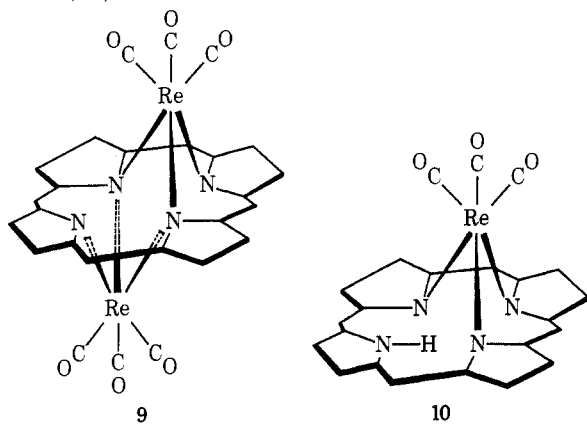
In the reported structure each rhenium atom is bonded to three of the nitrogen atoms in a distorted porphyrin ring. The metal–metal distance, though somewhat long for bonding,[64] is short enough that some interaction is a reasonable possibility.

These complexes can be used as models for two proposed metal-insertion intermediates. The monorhenium complex 10 resembles Fleischer's proposed "sitting atop complex" (11),[65] while the dirhenium complex 9 has been proposed by Hambright[66] as a model for another possible intermediate (12). The latter comparison may no longer apply, since the X-ray structure of 9 shows that both metal atoms lie off of the S$_2$ axis normal to the prophyrin plane. Alternately it might be concluded that intermediate 12 also has its two metal atoms located nonaxially.

11

12
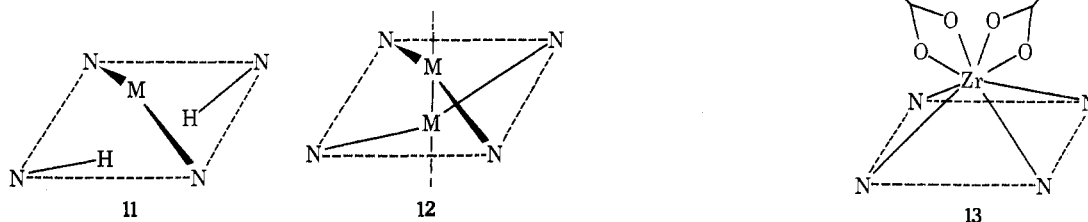
When Re(CO)$_5$Br is used instead of Re$_2$(CO)$_{10}$, a compound is obtained of stoichiometry Re$_2$(Por)-(CO)$_4$Br$_2$.[67] The diamagnetism of this complex is probably indicative of spin pairing between the two rhenium atoms, either in the form of a metal–metal bond or as superexchange through the porphyrin.

It has also been found[30] that technetium reacts in a manner similar to rhenium. A pair of technetium(I) porphyrins analogous to the rhenium(I) compounds have been prepared, as has a mixed complex μ-(Por)[Re(CO)$_3$][Tc(CO)$_3$].[68]

(63) D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Coord. Chem.*, 2, 101 (1972).

(64) D. Cullen, E. Meyer, T. S. Srivastava, and M. Tsutsui, *J. Amer. Chem. Soc.*, 94, 7603 (1972).

(65) E. B. Fleischer, E. I. Choi, P. Hambright, and A. Stone, *Inorg. Chem.*, 3, 1284 (1964).

(66) P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).

(67) M. Tsutsui and C. P. Hrung, to be published.

(68) M. Tsutsui and C. P. Hrung, *J. Amer. Chem. Soc.*, 95, 5777 (1973).

Heating a solution of monotechnetium complex causes disproportionation.[67] Disproportionation does

$$2[(PorH)Tc(CO)_3] \xrightarrow[\text{decalin}]{193°} PorH_2 + Por[Tc(CO)_3]_2$$
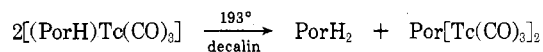
not occur with the monorhenium complex. A solution containing both uncomplexed porphyrin and ditechnetium complex shows no sign of the reverse reaction upon being heated. Apparently the monotechnetium complex, and by inference the monorhenium complex, are unstable. Only great kinetic inertness allows these novel mono complexes to be isolated.

Yoshida and coworkers[26] have used the carbonyl method to prepare a complex containing two rhodium atoms per porphyrin. It is thought that both rhodium atoms lie on the same side of the porphyrin plane and bond to each other through chloride bridges. However an X-ray structure determination will be necessary before this compound can be further discussed.

Further use of "novel" synthetic metalloporphyrins is expected in elucidating the geometries which axial ligands can assume. One approach would be to examine the metalloporphyrin complexes of metals known to exhibit coordination numbers greater than six. Scandium porphyrin forms complexes in which axially coordinated acetate or acetylacetonate acts as a bidentate ligand.[15] Considering the size and electronic structure of the metal and the steric requirement of the ligands, it is to be expected that the scandium is situated above the porphyrin plane. Zirconium(IV)[15] and hafnium(IV)[18,19] form porphyrin complexes each containing two bidentate acetate ligands. It has been proposed[15,19] that the metal atoms are also out of the porphyrin plane, thus coordinating both acetates on the same side of the porphyrin (13). This has been confirmed[69] by single crystal X-ray diffraction.


13

Metal–Carbon Bonds[70]

Since carbon–metalloid bonds occur commonly in nonporphyrin compounds, a metalloid porphyrin complex with a stable bond to carbon is not germane to this article. This is also true, to a lesser extent, for transition metal porphyrins containing cyanide or carbonyl ligands. However the presence of strong, neutral, π-acceptor ligands (*e.g.*, carbonyls, phosphines, and unsaturated hydrocarbons) is frequently required for transition metals to bond to alkyl, aryl, or acyl groups.[71] This type of organometallic bond is also formed in the presence of porphyrin or porphyrin-like ligands.

(69) J. L. Hoard, private communication.

(70) A more complete discussion of this topic is given by M. Tsutsui, *Proc. N. Y. Acad. Sci.*, in press.

(71) M. L. H. Green, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, p 203.

Alkyl and acyl complexes of cobalt porphyrins have been formed by oxidative addition to the appropriate Co(I) complex.[35] A second method, using a
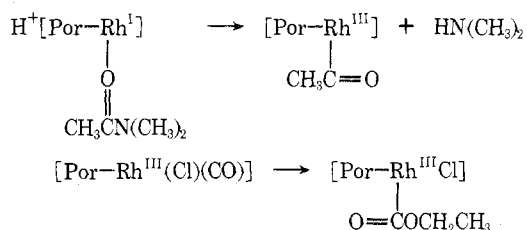
$$[Por-Co^I]^- + RX \xrightarrow[CH_3OCH_2CH_2OCH_3]{} [Por-Co^{III}R] + X^-$$
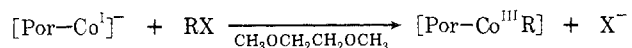
Grignard reagent, has been used to prepare alkyl and aryl cobalt porphyrin complexes by a nonoxidative route.[35] The two alkyl iron porphyrins reported[35] as

$$[Por-Co^{III}(py)(Br)] + RMgBr \longrightarrow$$
$$[Por-Co^{III}R] + MgBr_2 + py$$
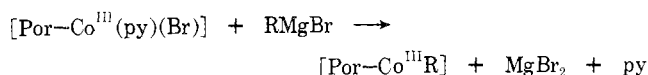
forming from iron(III) porphyrin and a Grignard reagent are less well characterized, the presence of alkyl ligands being based entirely on C, H, and N analyses.

An oxidative addition has also been used to prepare methyl rhodium porphyrin.[27] In this case the methyl group comes from an *N*-methylporphyrin (in a presumably intramolecular transfer) rather than from an alkyl halide. In addition, rhodium porphyrins have been reported to form acyl complexes, again by an intramolecular route.[72,73]

$$H^+[Por-Rh^I] \longrightarrow [Por-Rh^{III}] + HN(CH_3)_2$$

forming from iron(III) porphyrin and a Grignard reagent...

(structures: $CH_3CN(CH_3)_2$ with $C=O$; $CH_3C=O$)

$$[Por-Rh^{III}(Cl)(CO)] \longrightarrow [Por-Rh^{III}Cl]$$
$$O=COCH_2CH_3$$

The significance of alkyls of cobalt and rhodium porphyrins lies in their similarity to vitamin B_{12}, another compound forming metal–alkyl bonds from an M(I) species.[74] This resemblance is shared by several bidentate ligands,[75] pairs of which can assume a square-planar coordination geometry, and by a number of less well known macrocycles.[33]

Schrauzer[75] has ascribed the stability of these alkyls to the strong, planar ligand field of the porphyrin or porphyrin-like ligand. Consistent with this theory, Busch[33] found cobalt alkyl bonds to be stable only in the presence of macrocycles with greater than a certain minimum ligand field strength. Clearly nothing in these arguments should limit organometallic porphyrins to those of cobalt and rhodium. Nor is it obvious that rhodium porphyrins cannot undergo intermolecular addition and cobalt porphyrins, intramolecular addition. More work will be necessary to discover the scope of carbon–metal bonding in metalloporphyrins.

(72) B. R. James and D. V. Stynes, *J. Chem. Soc., Chem. Commun.*, 1261 (1972).
(73) I. A. Cohen and B. C. Chow, *Inorg. Chem.*, 13, 488 (1974).
(74) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, 5, 156 (1969).
(75) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968).

Chemically Induced Dynamic Electron Polarization of Transient Radicals

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One important application of electron spin resonance in chemical studies is in obtaining information on transient species produced in chemical reactions. A renewed and increasing interest in the field of free radical chemistry during the last decade can be attributed partly to the rapid development of electron spin resonance spectroscopy. Today esr has been developed to a point where much of the theoretical and experimental background material for chemists is readily available.

The first comprehensive and elegant demonstration of esr studies of transient radicals in liquid radiation chemical systems was by Fessenden and Schuler[1] in 1963. In that classic paper, the authors studied among other hydrocarbons the irradiation of liquid methane and deuteriomethane and reported the observation of both hydrogen and deuterium atoms. They noted that in both cases the low-field lines in the esr spectra are inverted compared to the corresponding high-field lines. This indicated that the low-field lines were not in the normal absorption

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(1) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).