Cytochrome P-450 Model Reactions, 3[◇]

Isolation and Characterization of a Porphinatomanganese(IV) Complex from the Reaction of Dichloro Monoxide with 5,10,15,20-Tetrakis-(2,6-dichlorophenyl)porphinatomanganese(III) Chloride [Mn(TDCPP)Cl]

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Received April 18, 1997

Keywords: Porphyrinatomanganese(IV) / Monooxygenase model / Dichloro monoxide / Catalytic alkene epoxidation / Catalytic alkane oxygenation / Catalytic alkane chlorination

The isolation at −78°C and characterization of the novel crystalline reactive porphinatomanganese(IV) complex Mn(TDCPP)$(OCl)_2$ (**5**) is described. **5** is compared with the porphinatomanganese(IV) complexes Mn(TDCPP)$(C_6H_5IOCl)_2$ (**2**), Mn(TDCPP)$(C_6F_5IOCl)Cl$ (**3**) and Mn(TDCPP)$(OCH_3)_2$ (**4**). The stoichiometric reaction of **5** with triphenylphoshane yields 2.5 equivalents of triphenylphosphane oxide and 1.0 equivalent of Mn(TDCPP)Cl (**1**). Complex **5** epoxidizes stilbene, and oxygenates and chlorinates cyclohexane.

In many organisms, cytochrome P-450 monooxygenases are responsible for a great number of biotransformations, by which one atom of the dioxygen molecule is transferred to substrates such as aliphatic and aromatic hydrocarbons, amines, and sulfides[2,3]. The cytochrome P-450 isozymes also play an essential role as phase-I detoxification enzymes[4] and furthermore are involved in cancer generation by metabolic activation of potential carcinogens such as benzene or benzo[*a*]pyrene[5].

Under anaerobic conditions, oxyen donors such as iodosylbenzenes, periodates, chlorites, hydroperoxides and peroxyacids are capable of substituting molecular oxygen in the oxygenation reactions of the cytochrome P-450 isozymes[6], resulting in the direct formation of the oxgenation-active species via the shunt pathway of the catalytic cycle[2]. In the active species, the iron has the oxidation state +IV. Substitution of iron by manganese in cytochrome P-450_{CAM} also leads to an active enzyme[7]. In vitro metalloporphyrins can be used as model compounds for these very complex enzymatic systems[2]. Thus, porphyriniron and -manganese complexes have been demonstrated to be efficient catalysts for the oxygenation of organic substrates in the presence of oxygen donors.

Monomeric, high-valent metal porphyrin complexes, which contain an activated oxygen atom capable of being transferred to alkanes or olefins can be regarded as analogous of the active state in the catalytic cycle of cytochrome P-450. Hence, information concerning the nature of the oxygenation-active species of the cytochrome P-450 isozymes can be gained by the isolation and characterization of active metalloporphyrin compounds. For such investigations, manganese offers an advantage over iron in that it is more stable in the higher oxidation states +IV and +V, thus making oxidized porphyrinmanganese complexes more easily accessible than the corresponding iron complexes. To date, only a few "active complexes" have been synthesized by the reaction of porphyrinmanganese(III) with the oxygen donors iodosylbenzene[8,9], hypochlorite[10,11], peroxyacids[11,12], peroxycarbonate[13], dimethyldioxirane[14], and pentafluoroiodosylbenzene[1].

Recently, oxygenations of substrates by porphyrinmanganese(III) complexes with the oxygen donor hypochlorite (bleach) have attracted interest due to their high efficiency[14]. Montanari et al.[16] demonstrated that in the two-phase system (water−hypochlorite/organic phase−substrate), the reaction rate considerably increases with a decrease in the pH of the aqueous phase from about 12.5 (bleach) to 9.5. They also demonstrated that by lowering the pH, the concentration of hypochlorous acid, which is in equilibrium with its anhydride, dichloro monoxide, and water[17], increases in the system. These findings prompted Rodgers and Goff[18] to investigate the systems [D_8]Mn(TPP)X/Cl_2O (TPP = *meso*-tetraphenylporphyrin) and [D_8]Mn(TMP)X/Cl_2O (TMP = *meso*-tetramesitylporphyrin) in solution (at −165 to −78°C) by means of ^{2}H-NMR and ESR spectroscopy. By variation of the reaction conditions in the system [D_8]Mn(TPP)X/Cl_2O, three spectroscopically distinct complexes were observed, one of which proved to be a manganese(IV) complex (S = 3/2) on the basis of its ESR spectrum.

Results and Discussion

We report herein on the isolation and characterization of the novel monomeric porphyrinmanganese(IV) complex

[◇] Part 2: Ref.[1].

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$Mn(TDCPP)(OCl)_2$ (**5**) and on a study of its capacity to act as an activated O- and Cl-transferring compound. At −78°C, Cl_2O does not react with Mn(TDCPP)Cl (**1**), hence **5** was prepared by the reaction of **1** with 3.5 equivalents of dichloro monoxide in dichloromethane at −10°C, with subsequent rapid cooling of the reaction mixture to −78°C to avoid decomposition of the sensitive product. Complex **5** precipitated as a blue-purple microcrystalline solid, which could be isolated by filtration at low temperature in a yield of 60%. At −60°C, **5** is soluble in chloroform and readily soluble in methyl acetate. In solution, conversion to the manganese(III) complex occurs within seconds at ambient temperature, or after several hours at −60°C.

For the preparation of **5**, the high oxidation stability of the TDCPP macrocycle, resulting from the strong electron-withdrawing effect of the eight chlorine atoms, is of importance. Under the aforementioned conditions of isolation, electron-rich porphyrin complexes such as Mn(TPP)Cl and Mn(TMP)Cl undergo rapid oxidative degradation in the presence of the reactive Cl_2O, as is evident from the disappearance of their characteristic UV/Vis bands. The chlorine substituents at the *ortho* positions of the phenyl groups in TDCPP also prevent the formation of μ-oxo dimers, due to their steric hindrance of the porphyrin plane[19].

Based on its elemental analysis and spectroscopic data, and the results of the stoichiometric reactions of **5** with triphenylphosphane (see below), we suggest the D_{4h}-symmetric structure shown in Figure 1 for complex **5**.

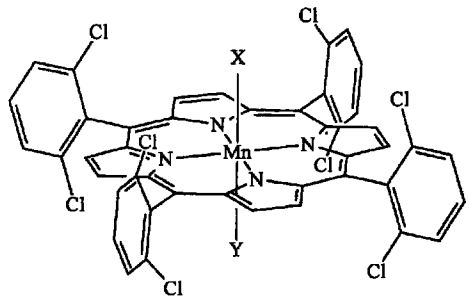
In the UV/Vis spectrum of complex **5**, a significant shift of the Soret band from λ = 478 to 416 nm with regard to the manganese(III) complex **1** can be observed. A similar shift was also noted for other porphyrinmanganese(IV) complexes that we have recently synthesized (see Table 1).

The FT-IR spectrum of **5** lacks the characteristic intense bands seen for **1**. The absence of an Mn−O−Mn oscillation at $\tilde{\nu}$ = 810 cm^{-1} confirms the monomeric structure of **5**[8,20].

The $^1H/^2H$-NMR signals of the pyrrole β-protons/deuterons in porphyrin complexes with paramagnetic metal centers tend to be significantly shifted out of the normal region of organic compounds (i.e. δ = 0−15) and are extremely broadened[21]. Moreover, the positions of these signals are strongly temperature-dependent (see Table 2). Due to the smaller gyromagnetic ratio of ^2H in comparison with ^1H (1:6.5), in the ^2H-NMR spectrum a substantial improvement of resolution as well as a significantly higher signal-to-noise ratio can be achieved[22]. In the ^2H-NMR spectrum of complex **5**, deuterated to 75% at the pyrrole β-positions, a single signal at δ = −37.0 is observed at −50°C, in accordance with the given structure. Compared with the deuterated complex [D_8]-**1**, the signal is slightly shifted to higher field and lies in the region characteristic for monomeric porphyrinmanganese(IV) complexes. The monomeric structure of **5** is clearly demonstrated by comparison with the $^1H/^2H$-NMR spectra of dimeric μ-oxo(porphyrin)manganese(IV) complexes with an antiferromagnetic coupling of the metal ions. The latter complexes undergo a partial saturation of spins across the oxygen bridge, so that the signals of the pyrrole β-protons lie in the region of δ = 7−8 and to not exhibit a strong broadening[8,20].

A dimeric μ-oxo structure can also be ruled out on the grounds of the x-band ESR spectrum of **5**, since dimeric

Figure 1



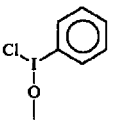
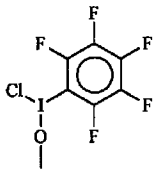
Complex		X	Y
1	$Mn^{III}(TDCPP)Cl$	Cl	–
2[8]	$Mn^{IV}(TDCPP)(C_6H_5IOCl)_2$	X = Y = 	
3[1]	$Mn^{IV}(TDCPP)(C_6F_5IOCl)Cl$		Cl
4[8]	$Mn^{IV}(TDCPP)(OCH_3)_2$	$O(CH_3)$	$O(CH_3)$
5	$Mn^{IV}(TDCPP)(OCl)_2$	OCl	OCl

Table 1. UV/Vis-spectroscopic data in CH_2Cl_2; **5** in methyl acetate

Complex	λ_{max} (lg ε) [nm]				
1	371 (4.791)	478 (5.140)	525 (3.740)	580 (4.086)	610 (3.699)
2		427 (4.981)	519 (4.159)	567 (3.623)	613 (3.489)
3		423 (4.858)	520 (3.899)		
4		421 (4.973)	530 (3.820)	590 (3.820)	
5	399 (sh)	416 (4.958)	515 (4.153)		

Table 2. β-Pyrrole ^2H-NMR signals of deuterated complexes

Complex	Solvent	T [°C]	δ (ppm)
1	$CDCl_3$	+25	−21.0 (s)[a]
1	$CDCl_3$	−50	−33.5 (s)[a]
[D_8]-1	CH_2Cl_2	+25	−22.0 (s)
[D_8]-1	CH_2Cl_2	−50	−35.2 (s)
[D_8]-1	Methyl acetate	−50	−33.2 (s)
[D_8]-3	CH_2Cl_2	−50	−33.9, −28.7, −26.8 (sh)
[D_8]-5	Methyl acetate	−50	−37.0 (s)

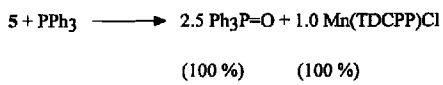
[a] ^1H-chemical shift of the non-deuterated compound.

complexes are ESR-inactive[8]. The ESR spectrum of **5** (measured as a polycrystalline solid at 20°C) is strongly anisotropic. An intense, broad signal (ca. 600 gauss) at $g_\perp$ = 5.16 (maximum, turning point not determinable) and a further, weak signal at $g_\parallel \approx 2.2$ with a distinct maximum at g = 3.1 and a minimum at g = 1.6 are observed, which is typical for monomeric manganese(IV) high-spin complexes (d^3) with a tetragonal distorted octahedral ligand field[23]. In contrast, manganese(IV) in a pure octahedral crystal field exhibits a single absorption at $g = 2$[24]. Likewise, porphyrin π radical cations also show a single, intense ESR absorption at $g \approx 2$[25].

The measurement of molar magnetic susceptibility by ^{1}H-NMR spectroscopy, as described by Evans[26], provides a useful method for the determination of the d-electron configuration in paramagnetic complexes[27]. In the case of **5** at −60°C, a value of $\chi_M = 11.57 \times 10^{-8}$ m^3/mol is found, from which the effective magnetic moment is calculated as μ_{eff} = 3.96 μ_B, confirming **5** as a manganese(IV) complex (theoretical value for a d^3-high-spin system, S = 3/2: μ_{eff} = 3.87 μ_B). In contrast, the manganese(III) complex **1** (d^4, S = 2) exhibits a molar magnetic susceptibility of χ_M = 12.58 × 10^{-8} m^3/mol at +20°C, resulting in an effective magnetic moment of μ_{eff} = 4.84 μ_B (theoretical value: μ_{eff} = 4.90 μ_B). The diamagnetic part of the porphyrin system itself makes a negligible contribution; the molar magnetic susceptibility of (TDCPP)H_2 at +20°C is $\chi_M = -0.38 \times 10^{-8}$ m^3/mol.

The stoichiometric reaction of **5** with triphenylphosphane yields quantitatively 2.5 equivalents of triphenylphosphane oxide and 1.0 equivalent of Mn(TDCPP)Cl (**1**).

Scheme 1

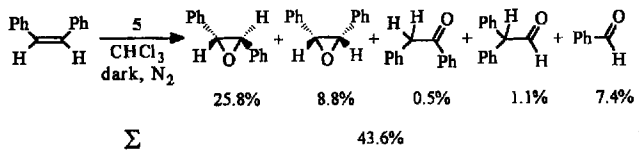


Two equivalents of triphenylphosphane oxide are produced by oxidation by the two axial OCl ligands, which each contain an oxygen atom with formally six electrons. The additional half equivalent results from the reduction of manganese(IV) to manganese(III).

Stoichiometric oxygenation reactions of hydrocarbons (*cis*-stilbene, cyclohexane) under anaerobic conditions demonstrate the suitability of **5** as a model compound for the terminal state in the catalytic cycle of cytochrome P-450 monooxygenases. In reactions with *cis*-stilbene, the main products are the *cis*- and *trans*-stilbene epoxides and benzaldehyde, which are formed alongside trace amounts of diphenylacetaldehyde and benzyl phenyl ketone. The overall yield of oxygenation products amounts to 43.6% and Mn(TDCPP)Cl is isolated quantitatively.

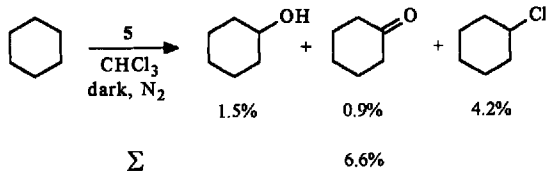
Compared to the reactions of the active complexes **2** and **3**, which we examined recently, the oxygenations with **5** proceed with an inverse stereospecificity; the average *cis*-epoxide/*trans*-epoxide ratio is 1:2.8 (cf. 7.6:1 for **2**[9], 3.5:1 for **3**[1]).

Scheme 2



In the stoichiometric reaction of cyclohexane with **5**, cyclohexanol, cyclohexanone and chlorocyclohexane are produced in an overall yield up to 6.6%.

Scheme 3



Both cyclohexanol and cyclohexanone originate from oxygen transfer from **5** to the substrate, whereas chlorocyclohexane is formed by transfer of activated chlorine from the OCl ligands. Thus, complex **5** exhibits chlorination activity towards substrates with non-activated C−H bonds in the dark. This finding is of interest since chloroperoxidase, which along with the cytochrome P-450 isozymes, belongs to the group of heme-thiolate enzymes and is believed to have the active state PFe(III)−O−Cl, only halogenates substrates with activated C−H bonds[6e,28]. The relatively low yields follow from the thermal sensitivity of complex **5**, which only reacts with the saturated substrate at somewhat elevated temperatures (monitored by UV/Vis control of the reaction mixture).

Experimental Section

General: All operations involved in the preparation of complex **5** were carried out under protective gas (argon or nitrogen) and with appropriately degassed solvents. Oxygenation reactions of **5** were additionally carried out under exclusion of light.

Instrumentation: NMR: Bruker AM 400. – FT-IR: Bruker IFS 88. – UV/Vis: Perkin-Elmer Lambda 2. – ESR: Varian E-3. – GC: Hewlett Packard 5890 Series II with FID and Ultra 2 capillary column (cross-linked 5% ph-me-silicon, 25 m). – Elemental analysis was carried out at the Analytische Laboratorien Malissa & Reuter, Gummersbach/Engelskirchen.

Materials: Chlorine (BASF), chlorobenzene (Janssen), chlorocyclohexane (Fluka), 4-chlorotoluene (Janssen), cyclohexane (Merck), cyclohexanol (BASF), cyclohexanone (Merck), ethyl acetate (Fluka), methanol (BASF), *cis*-stilbene (Merck). TLC plates Alox-100 UV_{254} (Macherey & Nagel). Chloroform was washed with concd. H_2SO_4 and water, dried with $CaCl_2$, and distilled. Dichloromethane was dried and distilled from CaH_2, pentane from LiH, and methyl acetate and carbon tetrachloride from potassium carbonate. Red mercury(II) oxide was activated by heating overnight at 110°C in a drying oven. Triphenylphosphane (BASF) was chromatographed on basic alumina (Fluka, 70–230 mesh, activity I).

Mn(TDCPP)Cl (**1**)[29] and dichloro monoxide[30] were prepared according to literature procedures; [D_8]Mn(TDCPP)Cl was prepared analogously to **1** using [D_5]pyrrole.

Preparation of Complex **5**: 0.3 g (0.307×10^{-3} mol) of Mn(TDCPP)Cl (**1**) was dissolved in 85 ml of dichloromethane and the resulting solution was filtered through a G4 glass-filter crucible into a two-necked flask to remove any undissolved residue. The solution was then cooled to −10°C and Cl_2O (1.07×10^{-3} mol, as a solution in CCl_4) was added. After stirring of the reaction mixture for 3 min at −10°C, it was rapidly cooled to −78°C. The mixture was stirred for a further 15 min, left for 1 h at −78°C, and the precipitate formed was filtered off by means of a glass-filter apparatus at −78°C. Residual solvents and excess Cl_2O were removed in vacuo (oil pump) at −50°C and the product was dried for 1 h at 20°C and 1 Pa, affording a blue-purple, microcrystalline solid, yield 0.18−0.2 g (56−62%). − UV/Vis (methyl acetate): λ_{max} (lg ε) = 399 nm (shoulder), 416 (4.958), 515 (4.153). − FT-IR (KBr): $\tilde{\nu}$ = 3940 cm^{-1}, 3850, 3742, 3103, 3079, 2836, 2739, 2543, 2357, 2253, 2175, 2032, 1941, 1868, 1807, 1651, 1579, 1557, 1541, 1504, 1428, 1332, 1305, 1255, 1229, 1203, 1191, 1154, 1107, 1078, 1007, 971, 901, 884, 835, 800, 778, 723, 701, 692, 663, 584, 497, 485, 465, 436, 422. − ESR (polycrystalline solid, ν = 9.17 GHz, 20°C): g = 5.16 (maximum, turning point not determinable), 2.2 (maximum at g = 3.1, minimum at g = 1.6). − Molar magnetic susceptibility ($CDCl_3$, −60°C): $\chi_M = 11.57 \times 10^{-8}$ m^3/mol. − ^{2}H NMR ([D_8]-**5** in methyl acetate, −50°C): δ = −37.0 (β-pyrrole-D). − $C_{44}H_{20}Cl_{10}MnN_4O_2$ (1046.14): calcd. C 50.52, H 1.93, Cl 33.89, Mn 5.25, N 5.36, O 3.06; found C 50.32, H 2.13, Cl 33.60, Mn 5.15, N 5.36, O 3.15. − Complex [D_8]-**5** was prepared as described above using [D_8]Mn(TDCPPMn)Cl.

Stoichiometric Reaction of Complex **5** *with Triphenylphosphane:* 0.125 g (0.12×10^{-3} mol) of complex **5** was dissolved in 70 ml of chloroform at −60°C. A cooled solution of triphenylphosphane (0.18 g, 0.7×10^{-3} mol) in 15 ml of chloroform was added and the stirred mixture was slowly allowed to warm to ambient temperature. The reaction products were then separated chromatographically on basic alumina (activity I). Excess triphenylphosphane was eluted with dichloromethane, triphenylphosphane oxide and Mn(TDCPPMn)Cl with dichloromethane/methanol (2:1). The latter fraction was concentrated to dryness and the residue was redissolved in 10 ml of dichloromethane. The insoluble portion of manganese(III) complex was removed by filtration and washed with dichloromethane until no more triphenylphosphane oxide was detectable in the washings by TLC. The components of the filtrate were then separated by preparative TLC (basic alumina/ethyl acetate). Mn(TDCPP)Cl remained at the baseline, while triphenylphosphane oxide exhibited an R_f value of 0.65. The appropriate bands were eluted with methanol, the extracts were filtered, and the solvent was completely removed from each. The residues were then dissolved in dichloromethane, the solutions were filtered once more, and residual Mn(TDCPP)Cl was combined with that collected before. After removing the solvents from the filtrates, the remaining residues were dried for 2 h at 110°C and the yields were determined by gravimetric analysis. The compounds were characterized by UV/Vis, IR and ^{1}H-NMR spectroscopy. The yield of triphenylphosphane oxide was additionally determined by ^{1}H-NMR spectroscopy after complete dissolution of the isolated material in $CDCl_3$ and addition of 4-chlorotoluene (50 µl, 0.423×10^{-3} mol) as an internal standard.

Oxygenation of cis-Stilbene and Cyclohexane with **5**: 0.125 g (0.12×10^{-3} mol) of complex **5** was dissolved in 70 ml of chloroform at −60°C. A cooled solutionof 1.0×10^{-3} mol of substrate in 5 ml of chloroform was then added and the stirred mixture was allowed to warm to ambient temperature over a period of 16 h. The solvent was then distilled off and the residue was extracted with 30 ml of pentane. The insoluble manganese(III) complex was removed by filtration and washed five times with pentane.

Reaction with cis-Stilbene: The pentane filtrates were combined and concentrated to dryness in a rotary evaporator at 30°C and 2×10^4 Pa. The residue was dissolved in a small volume of $CDCl_3$ and the yield was determined by ^{1}H-NMR spectroscopy after addition of 4-chlorotoluene (20 µl, 0.169×10^{-3} mol) as an internal standard.

Reaction with Cyclohexane: Due to the higher volatility of the products, the solvent of the combined filtrates was almost completely removed by distillation through a short Vigreux column after addition of chlorobenzene (10 µl, 0.098×10^{-3} mol) as internal standard. The yields of oxygenation products were determined by gas chromatography.

Characteristic ^{1}H-NMR Data (δ in $CDCl_3$) of the Oxygenation Products of **5**: 4-Chlorotoluene (internal standard): δ = 2.32 (s, 3H, methyl-H); triphenylphoshane: δ = 7.2−7.3 (m, 15H, aryl-H); triphenylphosphane oxide: δ = 7.5−7.8 (m, 15H, aryl-H); *cis*-stilbene: δ = 6.59 (s, 2H, olefin-H); *cis*-stilbene epoxide: δ = 4.30 (s, 2H, epoxide-H); *trans*-stilbene epoxide: δ = 3.82 (s, 2H, epoxide-H); diphenylacetaldehyde: δ = 9.80 (d, 1H, aldehyde-H); δ = 4.83 (d, 1H, methine-H); benzyl phenyl ketone: δ = 4.24 (s, 2H, methylene-H); benzaldehyde: δ = 10.0 (s, 1H, aldehyde-H).

CAS Registry Numbers: **1**: 91463-17-1, **2**: 117687-71-5, **3**: 143446-06-4, **4**: 117687-72-6, triphenylphosphane: 603-35-0, triphenylphosphane oxide: 791-28-6, *cis*-stilbene: 645-49-8, cyclohexane: 110-82-7, *cis*-stilbene epoxide: 1689-71-0, *trans*-stilbene epoxide: 1439-07-2, benzaldehyde: 100-52-7, diphenylacetaldehyde: 947-91-1, benzyl phenyl ketone: 451-40-1, cyclohexanol: 108-93-0, cyclohexanone: 108-94-1, chlorocyclohexane: 542-18-7.

[1] H. Volz, W. Müller, *Liebigs Ann.* **1992**, 1097−1101.
[2] P. R. Ortiz de Montellano (Ed.), *Cytochrome P-450*, Plenum Press, New York, **1986**.
[3] [3a] R. I. Murray, M. T. Fischer, P. G. Debrunner, S. G. Sligar in: *Metalloproteins* (Ed.: P. Harrison), part 1, VCH, Weinheim, **1986**, p. 157−206. − [3b] W. Kaim, B. Schwederski, *Bioanorganische Chemie*, Teubner, Stuttgart, **1991**, p. 114−134.
[4] F. P. Guengerich (Ed.), *Mammalian Cytochromes P-450*, vol. 2, CRC Press, **1987**.
[5] [5a] L. S. Alexander, H. M. Goff, *J. Chem. Educ.* **1982**, *59*, 179−182. − [5b] Y. Tagashira, T. Omura (Ed.), *P-450 and Chemical Carcinogenesis*, Plenum Press, new York, **1985**. − [5c] R. G. Harvey (Ed.), *Polycyclic Hydrocarbons and Carcinogenesis, Am. Chem. Soc.*, Washington, **1985**.
[6] [6a] E. G. Hrycay, P. J. O'Brien, *Arch. Biochem. Biophys.* **1972**, *153*, 480−494. − [6b] G. D. Nordblom, R. E. White, M. J. Coon, *Arch. Biochem. Biophys.* **1976**, *175*, 524−533. − [6c] F. Lichtenberg, W. Nastainczyk, V. Ullrich, *Biochem. Biophys. Res. Commun.* **1976**, *70*, 939−946. − [6d] J. A. Gustafson, E. G. Hrycay, L. Ernster, *Arch. Biochem. Biophys.* **1976**, *174*, 440−453. − [6e] J. H. Dawson, M. Sono, *Chem. Rev.* **1987**, *87*, 1255−1276.
[7] M. Gelb, W. A. Toscano Jr, S. G. Sligar, *Proc. Natl. Acad. Sci. USA* **1982**, *79*, 5758−5762.
[8] [8a] C. L. Hill, J. A. Smegal, B. C. Schardt, *J. Am. Chem. Soc.* **1983**, *105*, 3510−3515. − [8b] C. L. Hill, J. A. Smegal, *J. Am. Chem. Soc.* **1983**, *105*, 3515−3521.
[9] H. Volz, T. Barth, *Liebigs Ann.* **1989**, 171−175.
[10] B. Meunier, O. Bartolini, *J. Chem. Soc., Chem. Commun.* **1983**, 1364−1366.
[11] H. Volz, unpublished results.
[12] [12a] J. T. Groves, K. Stern, *J. Am. Chem. Soc.* **1987**, *109*, 3812−3814. − [12b] J. T. Groves, K. Stern, *J. Am. Chem. Soc.* **1988**, *110*, 8628−8638.
[13] [13a] M. Schappacher, R. Weiss, *Inorg. Chem.* **1987**, *26*,

1189–1190. – [13b] K. Ayougou, E. Bill, J. M. Charnock, C. D. Garner, D. Mandon, A. X. Trautwein, R. Weiss, H. Winkler, *Angew. Chem.* **1995**, *107*, 370–373; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 343–346.

[14] J. K. Kochi, S. Wolowiec, *J. Chem. Soc., Chem. Commun.* **1990**, 1782–1784.

[15] [15a] B. Meunier, *Chem. Rev.* **1992**, 1411–1456. – [15b] M. J. Gunter, P. Turner, *Coord. Chem. Rev.* **1991**, *108*, 115–161. – [15c] J. P. Collman, J. I. Brauman, P. D. Hampton, H. Tanaka, D. S. Bohle, R. T. Hembre, *J. Am. Chem. Soc.* **1990**, *112*, 7980–7984. – [15d] B. Meunier, *Bull. Soc. Chim. Fr.* **1986**, 578–594. – [15e] J. P. Collman, T. Kodadek, J. I. Brauman, *J. Am. Chem. Soc.* **1986**, *108*, 2588–2594. – [15f] J. P. Collman, B. Meunier, T. Kodadek, T. Hayashi, J. I. Brauman, S. A. Raybuck, *J. Am. Chem. Soc.* **1985**, *107*, 2000–2005. – [15g] B. Meunier, B. de Poorter, *Tetrahedron Lett.* **1984**, *25*, 1895–1896. – [15h] C. L. Hill, A. Smegal, T. J. Henly, *J. Org. Chem.* **1983**, *48*, 3277–3281. – [15i] B. Meunier, E. Guilmet, *Nouv. J. Chim.* **1982**, *6*, 511–513. – [15j] I. Tabushi, N. Koga, *Tetrahedron Lett.* **1979**, *20*, 3681–3684.

[16] F. Montanari, M. Penso, S. Quici, P. Vigano, *J. Org. Chem.* **1985**, *50*, 4888–4893.

[17] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter & Co. Berlin, **1964**, p. 122.

[18] [18a] K. R. Rodgers, H. M. Goff, *J. Am. Chem. Soc.* **1987**, *109*, 611–612. – [18b] K. R. Rodgers, H. M. Goff, *J. Am. Chem. Soc.* **1988**, *110*, 7049–7060.

[19] H. Volz, M. Hassler, H. Schäffer, *Z. Naturforsch.* **1986**, *41b*, 1265–1572.

[20] C. L. Hill, B. C. Schardt, F. J. Hollander, *J. Am. Chem. Soc.* **1982**, *104*, 3964–3971.

[21] G. N. LaMar, F. A. Walker Jensen in *The Porphyrins*, (Ed.: D. Dolphin), vol. 4, Academic Press, New York, **1978**.

[22] R. H. Holm, C. J. Hawkins in *NMR of Paramagnetic Molecules*, (Eds.: G. N. LaMar, W. Horrocks Jr., R. H. Holm), Academic Press, New York, **1973**, pp. 287.

[23] [23a] D. T. Richens, D. T. Sawyer, *J. Am. Chem. Soc.* **1979**, *101*, 3681–3683. – [23b] C. L. Hill, M. J. Camenzind, F. J. Hollander, *Inorg. Chem.* **1983**, *22*, 3776–3784.

[24] P. C. Moews, *Inorg. Chem.* **1966**, *5*, 5–8.

[25] [25a] I. Morishima, Y. Tokita, K. Yamaguchi, Y. Watanabe, *Inorg. Chem.* **1993**, *32*, 329–333. – [25b] W. R. Scheidt, B. Cheng, K. J. Haller, A. Mislankar, A. D. Rae, K. V. Reddy, H. Song, R. D. Orosz, C. A. Reed, F. Cuukiernik, J. C. Marchon, *J. Am. Chem. Soc.* **1993**, *115*, 1181–1183. – [25c] H. Fuji, *Inorg. Chem.* **1993**, *32*, 875–879.

[26] [26a] D. F. Evans, *J. Chem. Soc.* **1959**, 2003–2005. – [26b] S. K. Sur, *J. Magn. Reson.* **1989**, *82*, 169–173. – [26c] R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, **1986**, pp. 5.

[27] [27a] J. G. Hughes, P. J. Lawson, *J. Chem. Educ.* **1987**, *64*, 973–976. – [27b] R. Engel, D. Halpern, S. Bienenfeld, *Anal. Chem.* **1973**, *45*, 367–369.

[28] [28a] S. L. Neidleman, J. Geigert, *Biohalogenation: Principles, Basic Roles and Applications*, Ellis Horwood, Chichester, **1984**. – [28b] M. C. R. Franssen, H. C. van der Plas, *Bioorg. Chem.* **1987**, *15*, 59–70. – [28c] H.-A. Wagenknecht, W.-D. Woggon, *Angew. Chem.* **1997**, *109*, 404–407; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 390–392.

[29] [29a] W. Drenth, A. W. van der Made, E. J. H. Hoppenbruwer, R. J. M. Nolte, *Rec. Trav. Chim. Pays-Bas* **1988**, *107*, 15–16. – [29b] H. Kobayashi, T. Higuchi, Y. Kaizu, H. Osada, M. Aoki, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3137–3141. – [29c] A. D. Adler, F. R. Longo, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

[30] G. H. Cady in *Inorg. Synth.*, vol. 5 (Ed.: T. Moeller), McGraw-Hill, New York, **1957**, p. 156–165.

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