Russian Journal of General Chemistry, Vol. 71, No. 2, 2001, pp. 294–298. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 2, 2001, pp. 324–328.

Thermochemistry of Solution of Fe(III) and Mn(III) Complexes with Natural Porphyrins

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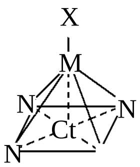
Received November 24, 1999

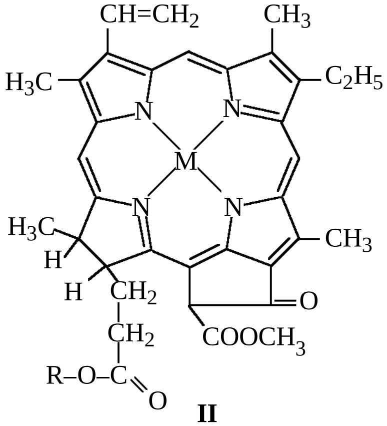
Abstract—The enthalpies of solution of Fe(III) and Mn(III) complexes with porphyrins of the chlorophyll group (chlorophyll ligand, pheophorbid, chlorin e_6) and protoporphyrin in various organic solvents at 298.15 K were determined calorimetrically. The influence of the structural features of porphyrin molecules and nature of the solvent on the enthalpy characteristics of porphyrin–solvent interaction was discussed.

The structural complexity and diversity of the structures of porphyrins and their metal complexes determine the specific features of their behavior in chemical reactions and physicochemical processes in solution. From the practical and theoretical viewpoint, it is urgent to develop a thermochemical approach to studying the properties of porphyrin molecules, in particular, the effect of metal, functional substituents, and solvent on the enthalpy characteristics of metal porphyrin– solvent interaction. In this connection, we measured calorimetrically at 298 K the enthalpies of solution of Fe(III) and Mn(III) complexes with porphyrins of various structures, that are structural models of bioporphyrins of these metals [1]. We took aprotic (benzene), proton-donor (chloroform), and proton-acceptor (DMF, pyridine, piperidine) solvents. Also, we calculated the relative enthalpies of interparticle interactions.

Iron(III) and manganese(III) porphyrins are inner-complex salts with a mixed coordination sphere. In contrast to Cu and Ni porphyrins [2], these complexes have a tetragonal-pyramidal structure with the base formed by four porphyrin nitrogen atoms and the apical position occupied by atom X (X = Cl^-, Br^-, O, etc.) (structure **I**). The Fe(III) or Mn(III) atom lies above the pyramid base at a distance of 0.2–0.5 Å [3–7]. The bonds of metal with the nitrogen atoms are largely covalent, whereas the bond with the axial ligand (Cl^-, Br^-, CN^-, Ac^-, etc.) is essentially ionic. The effective charge on the metal strongly differs from the formal charge. For example, on the Fe(III) atom in porphyrin complexes it is, on the average, as low as +0.26. The atoms of metal and anion are located at the ends of a dipole with the M–X distance of 2.19 (ClFeTPP), 2.22 (ClFePP), and 2.37 Å (ClMnTPP) [6, 7]. The M–X bond (X = Cl^-, Ac^-, etc.) can become a new center of solvation, absent in coordination-saturated metal porphyrins.

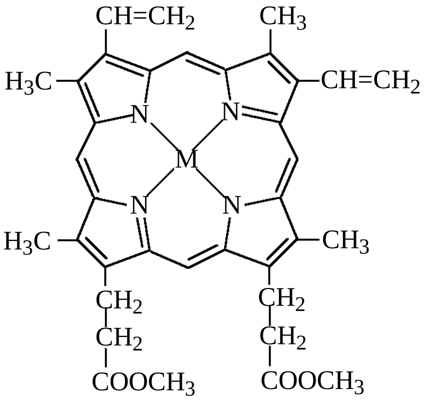


I
geometric structure of the coordination core



II

II, R = $C_{20}H_{39}$ (M-chlorophyll, MChP), CH_3 (M-pheophorbid, MPPb)



III

M-protoporphyrin (MPP)

From the viewpoint of coordination chemistry, the

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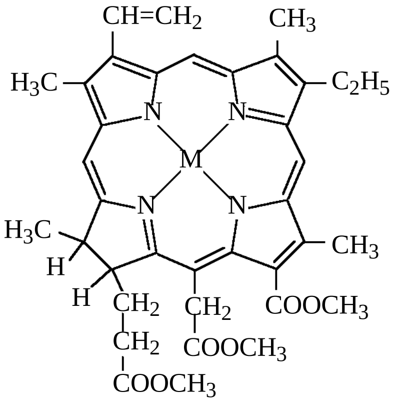
Table 1. Standard enthalpies of solution $\Delta_{soln}H^0$, kJ mol^{-1}, of metal porphyrins

Compound	C_6H_6	CCl_4	$CHCl_3$	DMF	C_5H_5N	$C_5H_{10}NH$
AcFeChP	7.5 ± 0.3	2.3 ± 0.1	–36.0 ± 0.5	–316.2 ± 2.0	–148.2 ± 1.5	–615.5 ± 3.5
AcFePPb	4.7 ± 0.3	5.8 ± 0.1	–31.6 ± 0.8	–98.4 ± 1.7	–97.8 ± 2.0	–365.8 ± 1.3
AcFeChn e_6	–8.7 ± 0.4	–	–8.7 ± 0.4	–54.5 ± 1.3	–48.8 ± 1.7	–
ClFePP	8.4 ± 0.5	–	–20.6 ± 1.5	–	–21.8 ± 1.2	–
AcMnChP	–35.9 ± 1.1	–	–83.6 ± 3.2	–97.0 ± 1.9	–114.1 ± 2.4	–679.4 ± 5.6
AcMnPPb	14.6 ± 0.9	–	–24.9 ± 1.4	–39.3 ± 1.6	–56.2 ± 2.6	–403.8 ± 6.3



IV

M-chlorin e_6 (MChn e_6)

Table 2. Standard enthalpies of transfer ($\Delta_{tr}H^0$, kJ mol^{-1}) of metal porphyrins from benzene

Compound	CCl_4	$CHCl_3$	DMF	C_5H_5N	$C_5H_{10}NH$
AcFeChP	–5.2	–43.5	–323.7	–155.7	–615.5
AcFePPb	1.1	–36.3	–103.1	–102.5	–370.5
AcFeChn e_6	–	–29.6	–45.8	–40.1	–
ClFePP	–	–29.0	–	–30.2	–
AcMnChP	–	–47.7	–61.1	–78.2	–643.5
AcMnPPb	–	–39.5	–53.9	–70.8	–418.4

Table 3. Standard enthalpies of solution ($\Delta_{soln}H^0$, kJ mol^{-1}) and of transfer ($\Delta_{tr}H^0$, kJ mol^{-1}, in parentheses) of porphyrin ligands [11]

Solvent	H_2ChP	H_2PPb	H_2Chn e_6	H_2PP
C_6H_6	30.6 ± 0.8	16.9 ± 0.8	14.2 ± 0.7	44.3 ± 0.8
CCl_4	22.5 ± 0.7	11.2 ± 0.7	–	–
	(–8.1)	(–5.7)	–	–
$CHCl_3$	1.3 ± 0.3	–9.2 ± 0.3	–2.2 ± 0.1	15.5 ± 0.7
	(–29.3)	(–26.1)	(–16.4)	(–28.8)
DMF	23.6 ± 0.5	8.0 ± 0.3	–10.3 ± 0.3	26.3 ± 0.5
	(–7.0)	(–8.9)	(–24.5)	(–18.0)
C_5H_5N	16.4 ± 0.9	8.6 ± 0.4	11.9 ± 0.9	30.6 ± 0.4
	(–14.2)	(–8.3)	(–2.3)	(–13.7)
$C_5H_{10}NH$	–35.9 ± 1.0	–53.8 ± 1.2	–25.8 ± 1.3	–
	(–66.5)	(–70.7)	(–40.0)	–

deviation of the central atom in metal porphyrins from the plane under the influence of the axial anion is due to three major factors [8]: stepwise formation of the axial complex, interaction of the force fields of the metal and the first incoming axial ligand X^-, and repulsion of the electron shells of the axial ligand from the π-electron shell of the porphyrin macroring. The relative contributions of these factors can differ depending on configuration of the porphyrin molecule and nature and charge of the metal and the axial ligand.

Since the metal atom in the complexes deviates from the plane, the sixth coordination site is shielded by the porphyrin nitrogen atoms (macrocyclic effect) [9, 10]. In strongly coordinatingd solvents (DMF, pyridine, piperidine) the Cl^- or Ac^- anions can be displaced to the outer sphere, and the electron-donor solvent molecules can occupy the sixth site as extra ligands (a sort of additional solvation).

In Tables 1 and 2 are given the standard enthalpies of solution and relative solvation (transfer from benzene) of the Fe(III) and Mn(III) complexes with the selected porphyrins. The experimental data show that $\Delta_{soln}H^0$ of metal porphyrins in noncoordinating solvents is lower than that of the corresponding ligands (Table 3), which is due to the lower energy of the crystal lattice, because the pyramidal structure of the complexes prevents intermolecular interactions in the crystal. Apparently, the crystal lattice of AcMnChP (**II**) is particularly loose, as this compound dissolves with an exothermic effect (–35.9 kJ mol^{-1}) even in benzene. Acetate ion as the ionic axial ligand in this metal porphyrin strongly affects the state of the Mn–X bond, which is manifested in the bathochromic shift of the first absorption band in the electronic spectrum

Table 4. Position and intensity (log ε) of the first absorption band in the electronic absorption spectra of the Fe(III) and Mn(III) pophyrin complexes

Solvent	C_6H_6	$CHCl_3$	DMF	C_5H_5N	$C_5H_{10}NH$
AcFeChP	627 (3.95)	628 (4.13)	612[a] (3.48)	615 (3.72)	628[a] (3.48)
AcFePPb	624 (3.78)	626 (4.01)	–	641 (3.80)	637[a] (3.19)
ClFePP	635 (3.73)	638 (3.69)	588 (3.74)	633 (3.34)	–
AcMnChP	715 (3.38)	693 (3.36)	683 (3.40)	690 (3.83)	641 (3.80) Decomposes
AcMnPPb	673 (4.25)	672 (4.44)	669 (4.18)	670 (4.23)	669[b]
AcFeChn e_6 (Soret band)	417	413	402	422	417
H_2ChP	670	668	668	670	664
H_2PPb	670	668	668	670	666

[a] The Soret band is blurred. [b] The Soret band is weak.

Table 5. Enthalpies of interaction of Fe(III) and Mn(III) porphyrins with organic solvents ($\Delta_{int}H^0$, kJ mol^{-1})

Metal porphyrin	CCl_4	$CHCl_3$	DMF	C_5H_5N	$C_5H_{10}NH$
(OAc)FeChP	2.9	–14.2	–316.7	–141.5	–556.5
(OAc)FePPb	6.1	–10.3	–94.2	–94.2	–299.8
(OAc)FeChn e_6	–	–13.2	–21.3	–37.8	–
ClFePP	–	–0.2	–	–16.5	–
(OAc)MnChP	–	–18.4	–54.1	–64.0	–557.0
(OAc)MnPPb	–	–13.5	–45.0	–62.5	–347.7

in benzene ($\Delta\lambda_1$ 45.6 nm) relative to chlorophyll ligand (Table 4). In the case of AcMnPPb, the bathochromic shift $\Delta\lambda_1$ is as small as 2.6 nm, and $\Delta_{soln}H^0$ is positive (14.6 kJ mol^{-1}). It is yet unclear why the effect of the phytol substituent in Mn(III) complexes with chlorophyll ligand and pheophorbid on the enthalpy characteristics of solution is so strong, as in the Fe(III) complexes in noncoordinating solvents its effect is less significant.

Analysis of the enthalpies of transfer (Table 2) suggests that the phytol substituent in Fe(III) and Mn(III) chlorophyll complexes enhances their solvation with noncoordinating solvents (CCl_4, $CHCl_3$), and the enthalpies of transfer become more negative by 6–8 kJ mol^{-1} on the average.

Boucher [6] reports for Fe(III) porphyrin complexes the Fe–Cl distance of 2.19 Å (data for Ac^- are lacking), which is considerably shorter than the sum of the Fe and Cl ionic radii and suggests significant axial interaction. It is also noted in that paper that, when forming complexes with molecular ligands having strong σ-electron donor power, Fe(III) porphyrin complexes can pass to the low-spin state, whereas for Mn(III) porphyrins no spin coupling is known. These data suggest that the porphyrin ligand in the Mn complex is bound more strongly than in Fe(III) complexes. By analogy, we can suggest that the manganese–porphyrin covalent bonding decreases the positive effective charge on the metal and increases δ^- on the axial Ac^-, which, in turn, should result in stronger specific solvation of Ac^- with chloroform. Indeed, the enthalpies of interaction ($\Delta_{int}H^0$) of chloroform with the metal porphyrin, calculated from data in Tables 2 and 3 by the equation $\Delta_{int}H^0 = \Delta_{tr}H^0_c - \Delta_{tr}H^0_l$ ($\Delta_{tr}H^0_c$ and $\Delta_{tr}H^0_l$ are the enthalpies of transfer of the complex and ligand, respectively), for AcMnP are by 3–4 kJ mol^{-1} more negative than for AcFeP. The phytol residue in the metal complexes of chlorophyll ligand also increases $\Delta_{int}H^0$ by 3–4 kJ mol^{-1} (Table 5).

The features of specific solvation of the complexes (X)MnP and (X)FeP with electron-donor solvents are determined by the nature of the axial ligand (X^- anion), distance by which the M^{3+} cation is displaced from the N_4 coordination plane (M–Ct distance), and nature of the coordination bonds M–N and M–L, where L is a molecular ligand. Lomova [12] correlates the higher kinetic stability of Mn(III) tetraphenylporphine complexes, as compared to Fe(III) analogs, with the stronger donor–acceptor interaction M–N and the $M \leftarrow N$ π bonding. The IR spectra of these complexes suggest appreciable contribution of the π component to the M–N bonds only for the Mn(III) complex. In covalent high-spin complexes of Mn^{3+} with porphyrins, there are favorable conditions for formation of the M–N π bond with filling of *d* orbitals and formation of the stable d^5 configuration. The Fe^{3+} ions already have stable half-filled t^3_{2g} and $t^3_{2g}l^2_g$ orbitals. Therefore, the $M \leftarrow N$ π bonding is more probable in AcMnTPP than in AcFeTPP. These facts support the above reasonings concerning the specific features of solvation of Fe(III) and Mn(III) complexes with proton-donor chloroform.

Table 1 shows that the complexes under consideration, except AcFeChn e_6, dissolve in electron-donor solvents (DMF, pyridine, piperidine) with large or very large negative heats of solution. Apparently, in this case dissolution in solvents with a high donor number (*DN*) is accompanied by side processes affecting the molecular structure, which is manifested in the electronic absorption spectra (Table 4).

V'yugin [13] also gives attention to large negative heats of specific solvation of (X)MnTPP in piperidine. Other processes, along with extra coordination of piperidine molecules, are suggested to occur. Karmanova *et al*. [14] have examined the ESR and electronic absorption spectra of the complexes (X)MnTPP in piperidine and concluded that under these conditions the manganese oxidation state changes from Mn(d^4) to Mn(d^5); it is noted that the Mn(d^5) state in porphyrin complexes is unstable and exists only in strongly electron-donor media. In this state the central atom can take up two molecular ligands.

Comparison of the enthalpies of interaction ($\Delta_{\text{int}}H^0$) of Fe(III) and Mn(III) porphyrin complexes with electron-donor solvents (Table 5) and the electronic absorption spectra shows that very large values of $\Delta_{\text{int}}H^0$ of AcFeChP with DMF and pyridine and of AcFePPb, AcMnChP, and AcMnPPb with piperidine correlate with significant changes in the spectra. For example, a solution of AcMnChP in piperidine has an absorption band at 474 nm only, and the Soret band (about 400 nm) is absent, which suggests decomposition of the macrocycle. In some cases (AcFeChP in DMF, AcFeChP, AcFePPb in piperidine), the Soret band is blurred and weak. In the spectrum of AcFePPb in DMF, the Soret band is present but the remaining part of the visible spectrum is not resolved.

In the chemistry of chlorophyll and its analogs with other metals, reactions are known involving intramolecular oxidation of the macrocycle with cleavage of the cyclopentanone ring or complete breakdown of the macrocycle [15]. An example is the so-called Molish phase test: Addition of an alkaline agent to a solution of chlorophyll or its derivative containing a cyclopentanone substituent leads first to appearance and then to disappearance of a color [16]. A similar phenomenon was described in [17], namely: In reaction of $FeCl_3$ with chlorophyll, a brown color first appears and then disappears. This is due either to cleavage of the cyclopentanone ring only or to total degradation of the molecule. It is interesting that the reaction with $FeCl_3$ is known from the analytical chemistry as a qualitative reaction for phenols. In the reaction of $FeCl_3$ with chlorophyll, the ketone group apparently transforms into the enol group, which reacts with $FeCl_3$ similarly to phenols, insofar as the enol form of chlorophyll is an analog of phenols.

Studies of protolytic dissociation of some chlorophyll complexes in strong proton-donor media revealed cases when the metal ion is released from the complex and the ligand macrocycle in the transition state is broken down [15]. Apparently, the process observed with the Fe(III) and Mn(III) complexes in piperidine and DMF (Table 4) is intramolecular breakdown of the macrocycle. Molecular oxygen may also exert certain effect on the process, as the phytol substituent containing a π bond can facilitate oxidative transformations. This assumption is confirmed by the significantly larger negative value of $\Delta_{\text{int}}H^0$ of Fe(III) and Mn(III) complexes with chlorophyll ligand in piperidine as compared with the pheophorbid complexes containing no phytol substituent. In the other cases, when dissolution of metal porphyrins in electron-donor solvents is not accompanied by essential changes in the electronic spectra, the increase in $\Delta_{\text{int}}H^0$ as compared to noncoordinating solvents is due to specific solvation of the central atom of the metal porphyrin with solvent molecules.

To check this interpretation, we studied the thermochemistry of solution of the Fe(III) chlorin e_6 complex in various solvents. Chlorin taken as trimethyl ester **IV** contains no phytol substituent and no cyclopentanone ring. Table 5 shows that the enthalpy characteristics of interaction of AcFeChn e_6 with electron-donor solvents are related to specific solvation of the central atom without side reactions, similar to ClFePP.

EXPERIMENTAL

Porphyrin ligands for synthesis of Fe(III) and Mn(III) complexes were prepared as described in [18, 19]. Acetatoiron(III) porphyrins were prepared by heating (90°C, 1–2 h) the corresponding porphyrin ligand with a tenfold molar excess of iron powder in acetic acid. The reaction completion was judged from the disappearance of the bands of the initial ligand from the electronic absorption spectrum. The solvent was distilled off in a vacuum, and the residue was dissolved in chloroform, filtered, and chromatographed on alumina (Brockmann grade IV) with chloroform as eluent. The eluate was evaporated, and the complex was precipitated with hexane. Chloroiron(III) porphyrins were prepared by heating $FeCl_2$ with the corresponding ligand in chloroform–methanol (1 : 1) in an inert atmosphere. Manganese(III) porphyrin complexes were prepared from Mn(II) acetate and porphyrin ligand in acetic acid as described for acetatoiron(III) porphyrins. The electronic absorption spectra (band positions and intensities) of the products agreed with published data [6, 20].

The enthalpies of solution were determined on a precision calorimeter with a variable-temperature isothermal jacket [21]. Prior to experiments, samples were finely divided and vacuum-dried at 350 K to constant weight. The electronic absorption spectra were taken on a Specord M-40 spectrophotometer. Organic solvents were purified as described in [22]. The experimental data and calculation results are listed in Tables 1–5.

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