Some Mn^III-porphyrins with de-polymerization activity toward humic acid

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Some Mn^{III}-porphyrins with de-polymerization activity toward humic acid

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Four Mn^{III}-porphyrin complexes, chloro(tetraphenylporphinato)Mn^{III}(1,6-diaminohexane), bromo(tetraphenylporphinato)Mn^{III}(1,6-diaminohexane), azido(tetraphenylporphinato)Mn^{III} (1,6-diaminohexane), and thiocyanato(tetraphenylporphinato)Mn^{III}(1,6-diaminohexane), have been synthesized. These complexes have been characterized using UV-Vis, IR, ESI-mass spectra, elemental analyses, magnetic susceptibility measurements, and conductivity measurement. The molar conductance values of these complexes in ethanol indicate non-electrolytes. The utility of these complexes in de-polymerization of coal using humic acid as the coal model has been tested by the optical density method.

Keywords: Mn^{III} porphyrins; 1,6-Diaminohexane; Humic acid; De-polymerization activity; Optical density method

1. Introduction

The increasing demand for catalysts in oxidation reactions under mild conditions has provided the impulse for research into new efficient systems based on metalloporphyrin catalysts that mimic natural enzymatic systems [1–10]. Manganese peroxidase is a heme containing enzyme secreted by fungal strains [11–13], which oxidizes Mn^{II} to Mn^{III} in the presence of H_2O_2. The enzyme generated Mn^{III} is stabilized by chelators such as oxalate, which also are secreted by the fungi [14]. Mn-peroxidase de-polymerizes lignin, which is a natural polymer of varying composition containing aryl propyl unit [15]. Humic acid has structural similarity with lignin and is considered as a coal model. There is interest in developing catalysts which can de-polymerize high molecular mass coal fraction to low molecular mass fraction so that it could be used as a feedstock for production of commodity and rare chemicals as an alternative to depleting oil reserves which are at present the basis of our chemical industries. It has been shown that Mn-peroxidase de-polymerizes humic acid [16] and this de-polymerizing activity is due to the Mn^{III}-chelated complexes. Our interest in the synthesis and characterization of Mn^{III}-porphyrin complexes [17] for various applications has prompted us to synthesize some Mn^{III}-porphyrin complexes and to see if they can de-polymerize humic acid so that we can modify those complexes and use them for de-polymerization of high

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molecular mass fraction of coal. Of the four Mn^{III}-porphyrin complexes which we report in this manuscript, three have been found to de-polymerize humic acid in the same way as Mn-peroxidase.

2. Experimental

2.1. *Materials*

All the chemicals which have been used were of A.R. grade and have been purified and dried whenever necessary by standard methods [18–20]. Pyrrole was purchased from Merck (Germany) and acetylacetone from S.D-Fine Chemicals (Mumbai). Pyrrole and acetylacetone were freshly distilled.

Humic acid was in the form of its sodium salt and purchased from Aldrich. Milli-Q water has been used throughout the experimental procedure. The stock solution of humic acid was prepared in Milli-Q water $1 \, mg \, mL^{-1}$ while the complexes have been used in $10^{-3} \, mol \, L^{-1}$ concentration.

2.2. *Physical measurements and methods*

The complexes were analyzed using standard procedures [21]. Elemental analyses have been done from Cochin University of Science and Technology, Cochin. Electronic spectra were recorded on Hitachi (Japan) model U-2000. IR spectra were recorded on a Perkin-Elmer (model-557) Beckman-Acculab-10. The magnetic susceptibility measurements were carried out at room temperature using EV7 VSM (ADE-DMS-USA) Vibrating Sample Magnetometer from IIT, Kanpur. Conductivity measurements were carried out on a century digital conductivity meter, model cc-601, with $10^{-3} \, mol \, L^{-1}$ concentration in ethanol. ESI-mass spectra were recorded on WATERS-Q-T of premier-HAB213 using ethanol as a solvent, from IIT Kanpur. Purity of the complexes was checked by TLC using CH_2Cl_2/CH_3OH in $1:4$ volume ratio as the solvent.

The absorbance was recorded on the same spectrophotometer as mentioned above using 1 mL capacity cuvettes at room temperature. The de-polymerization activity of these complexes has been assessed by measuring the increase in absorbance at 360 nm and decrease in absorbance at 450 nm [22, 23]. The reaction solution consisted of 20 μL of humic acid solution and 892 μL of Milli-Q water. The reaction was initiated by addition of 88 μL of Mn^{III}-porphyrin solution. Absorbance was observed at the intervals of 30 s at 360 nm and 450 nm, respectively. Absorbance *versus* time graphs were made at 360 nm and 450 nm.

2.3. *Syntheses*

2.3.1. Synthesis of Mn^{III}-porphyrins, [Mn^{III}(TPP)X]. The ligand, meso-tetraphenylporphyrin was synthesized by a known method [24]. The synthesis of Mn^{III}-porphyrins was carried out by adopting combined literature methods [25, 26]. The bis (acetylacetonato) Mn^{III} complexes with axial halo- or pseudohalo groups, i.e. Cl$^-$,
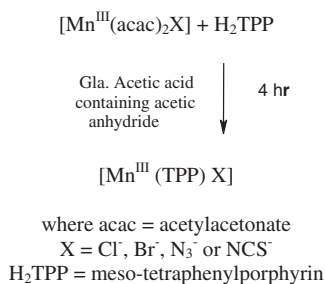
Br$^-$, NCS$^-$, or N$_3^-$, serve as useful synthetic intermediates for the synthesis of Mn^{III}-porphyrins [27].

For the synthesis of [Mn^{III}(TPP)NCS], 1.24 g (0.004 mole) of [Mn^{III}(acac)$_2$NCS] and 2.5 g (0.004 mole) of H$_2$TPP ligand were dissolved in 150 mL of glacial acetic acid containing 45 mL of acetic anhydride. Then the whole solution was refluxed for 4 h on a hot plate. After refluxing, it was evaporated to dryness on a steam-bath. The resulting shining blue colored metal complex was dissolved in minimum CHCl$_3$ to recrystallize and was finally dried under vacuum. Yield was 2.80 g (75%). Other complexes were prepared under similar conditions.

2.3.2. Synthesis of 1,6-diaminohexane complexes, [Mn^{III}(TPP)X(dah)]. For the synthesis of [Mn^{III}(TPP)NCS(dah)], 0.725 g (0.001 mol) of [Mn^{III}(TPP)NCS] was dissolved in 4.0 mL of ethanol and then 1.8 g (0.015 mole) of 1,6-diaminohexane was added. The whole content was stirred for 25 min at room temperature, then refluxed for 43 h. The reaction mixture was cooled at room temperature for 1 h and dried under vacuum over P$_2$O$_5$. Recrystallization was done with ethanol. The obtained yield was 0.400 g (48%). The other complexes were prepared analogously. All these complexes were hygroscopic.

3. Results and discussion

Mn^{III} complexes with the porphine ligand were synthesized by the following reaction scheme:

$$[Mn^{III}(acac)_2X] + H_2TPP$$

Gla. Acetic acid containing acetic anhydride $\quad\downarrow\quad$ 4 hr

$$[Mn^{III}(TPP)X]$$

where acac = acetylacetonate
X = Cl$^-$, Br$^-$, N$_3^-$ or NCS$^-$
H$_2$TPP = meso-tetraphenylporphyrin

These [Mn^{III}(TPP)X] complexes were dissolved in ethanol and refluxed with 1,6-diaminohexane to give [Mn^{III}(TPP)X(dah)]. The proposed reaction scheme may be given as

$$[Mn^{III}(TPP)X] + dah$$

EtOH $\downarrow$ 24 h

$$[Mn^{III}(TPP)X(dah)]$$
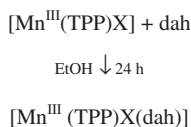
where dah = 1,6-diaminohexane.

All these complexes were soluble in ethanol, methanol, pyridine, chloroform, DMSO, DMF, and moderately soluble in water. The molar conductances of these complexes in ethanol at 10^{-3} mol L^{-1} are 9–16 Ω^{-1} cm^2 mol^{-1}, indicating non-electrolytes [28]. Physical properties of these complexes are given in table 1.

Table 1. Physical properties of Mn^{III}-porphyrins.

| Complexes | μ_{eff} | Molar conductance | Yield (%) | Color | Analysis found (Calcd) % | | | | | | Formula weight |
					C	H	N	S	Br	Cl	Mn	
[Mn(TPP)Cl(dah)]	4.93	15	33	Brown	73.28 (73.22)	5.41 (5.35)	10.26 (10.20)	–	–	4.32 (4.30)	6.70 (6.65)	818
[Mn(TPP)Br(dah)]	4.98	12	68	Brown black	69.50 (69.41)	5.13 (5.09)	9.73 (9.63)	–	9.25 (9.22)	–	6.36 (6.30)	863
[Mn(TPP)N$_3$(dah)]	4.95	9	43	Brown purple	72.69 (72.59)	5.37 (5.31)	15.27 (15.23)	–	–	–	6.65 (6.62)	825
[Mn(TPP)NCS(dah)]	4.91	16	84	Brown purple	72.73 (72.60)	5.27 (5.18)	11.65 (11.56)	3.81 (3.69)	–	–	6.52 (6.50)	841

3.1. *IR spectra*

IR spectra of these complexes show sharp bands at $\sim 1622 \, cm^{-1}$, suggesting $\nu(C=C)_{Pyrrole}$. A medium band at $\sim 1326 \, cm^{-1}$ for $\nu(C=N-)$ appears at $1350 \, cm^{-1}$ in the free ligand, a downward shift of $\sim 25 \, cm^{-1}$ due to coordination of porphyrins. Another medium band is at $\sim 1179 \, cm^{-1}$ for $\nu(C-N)$. A medium band at $\sim 1571 \, cm^{-1}$ indicates $\nu(C=C)_{phenyl}$. A broad band at $\sim 3020 \, cm^{-1}$ shows $\nu(C-H)_{phenyl}$. A sharp band at $\sim 980 \, cm^{-1}$ indicates (C–H) rocking mode of pyrrole. All these peaks of the porphyrin are in agreement with literature values [29]. The spectrum of thiocyanato (meso-tetraphenylporphinato) Mn^{III} has two characteristic bands of coordinated NCS^-, $\nu(C-S)$ at $836 \, cm^{-1}$ and $\nu(C-N)$ at $2095 \, cm^{-1}$. The observed value at $836 \, cm^{-1}$ falls in the region expected for N-bonded NCS^- $(860–780 \, cm^{-1})$ [30], confirming that NCS coordinates through N. Two characteristic peaks are observed in the azido(meso-tetraphenylporphinato) Mn^{III} complex for coordinated azide assigned as $\nu_{as}(N-N)$ showing strong absorption at $1252 \, cm^{-1}$ which usually appears from 1340 to $1180 \, cm^{-1}$ and another broad peak at $2030 \, cm^{-1}$, indicating coordination of N_3^- [31]. All these Mn^{III}-porphyrins exhibit a medium band at $\sim 465 \, cm^{-1}$ for $\nu(Mn-N)$ [32, 33] in their IR spectra.

The $\nu(NH_2)$ of 1,6-diaminohexane are at ~ 3422 and $\sim 3315 \, cm^{-1}$ for free and coordinated amine, respectively. Characteristic bands of diamines appear between 1400 and $700 \, cm^{-1}$. A strong band is observed at $\sim 1325 \, cm^{-1}$ assigned to $\omega \, (NH_2)$. The CN stretch of all uncomplexed diamines are at $1090–1070 \, cm^{-1}$ [34]. In these newly synthesized complexes, bands are at $1055–1046 \, cm^{-1}$. This shift indicates coordination of nitrogen to manganese. The NH_2 rocking mode is a strong band at $\sim 635 \, cm^{-1}$. The $\nu(C-C)$ has been assigned as a strong band at $\sim 1000 \, cm^{-1}$ [35]. The above data indicate that 1,6-diaminohexane coordinates unidentate to Mn^{III} (table 2).

3.2. *Electronic spectra*

Electronic spectra of the porphyrins exhibit an intense band at 400 nm that are assigned as Soret or B band. Several weaker absorptions also occur at 480–700 nm, which are known as Q bands.

For $[Mn^{III}(TMPP)X(en)]$ [17], the B bands appear with $\lambda_{max}(nm)$ at 427, 431, 435, and 440 and Q bands with $\lambda_{max}(nm)$ at 651, 625, 652, and 604, where $X=Cl^-$, Br^-, N_3^-,

Table 2. Selected vibrational frequencies (cm^{-1}) of Mn^{III}-porphyrins.

[Mn(TPP)Cl(dah)]	[Mn(TPP)Br(dah)]	[Mn(TPP)N₃(dah)]	[Mn(TPP)NCS(dah)]	Assignment
455	472	465	465	$\nu(Mn-N)$
1618	1620	1620	1620	$\nu(C=C)_{Py}$
1315	1308	1313	1315	$\nu(C=N)$
1176	1154	1178	1175	$\nu(C-N)$
1551	1550	1550	1553	$\nu(C=C)_{ph}$
3005	2923	2975	2970	$\nu(CH)_{ph}$
–	–	–	2080	$\nu(NCS)$
–	–	2030	–	$\nu(N_3)$
3320	3314	3328	3320	$\nu(NH_2)_{coordinated}$
3422	3421	3422	3422	$\nu(NH_2)_{uncoordinated}$

Table 3. UV-Vis spectroscopic data of free porphyrin and Mn^{III}-porphyrins.

Ligand/Complexes	λ_{max} (nm)	
	Soret band	Q Band
H$_2$TPP	406	647
[Mn(TPP)Cl(dah)]	449	666
[Mn(TPP)Br(dah)]	445	665
[Mn(TPP)N$_3$(dah)]	460	678
[Mn(TPP)NCS(dah)]	455	666

Table 4. Ligand field parameters calculated for Mn^{III}-porphyrins.

Complexes	$10D_q$ (cm^{-1})	B (cm^{-1})	β
[Mn(TPP)Cl(dah)]	22,271	824	0.72
[Mn(TPP)Br(dah)]	22,471	832	0.72
[Mn(TPP)N$_3$(dah)]	21,739	804	0.70
[Mn(TPP)NCS(dah)]	21,978	813	0.71

and NCS$^-$, respectively. In our case, these Mn^{III}-porphyrins with 1,6-diaminohexane exhibit B bands with λ_{max}(nm) at 449, 445, 460, and 455, while the Q bands appear with λ_{max}(nm) at 666, 665, 678 and 666 for the Cl$^-$, Br$^-$, N$_3^-$, and NCS$^-$ complexes, respectively (table 3). The assignment of B band has been done on the basis of earlier studies [36, 37].

Thus, all data for these newly synthesized Mn^{III}-complexes with H$_2$TPP and 1,6-diaminohexane follow similar trends when compared with [Mn^{III}(TMPP)X(en)]. The intense band at 445–460 nm in spectra of these complexes are assigned to charge transfer from a$_{1u}(\pi)$ and a$_{2u}(\pi)$ of porphyrin to e$_g$(dπ) orbital of manganese [38–40]. The ligand field parameters, i.e. $10D_q$, B, and β, have also been calculated for these Mn^{III}-porphyrins. The values of $10D_q$ have been calculated from λ_{max} at maximum absorbance. The value of B has been calculated by using the formula $D_q/B = 2.7$ using the Tanabe–Sugano diagram, while β has been calculated using the formula:

$$\beta = B_{\text{in complex}}/B_{\text{Free ion}}.$$

The values of B are below the free ion value for Mn^{III} (1140 cm^{-1}) [41] indicating covalent metal ligand bonds, with the covalency factor β of 0.71 ± 0.01 (table 4).

3.3. *Magnetic susceptibility*

Magnetic susceptibility measurements show that these complexes have μ_{eff} values of 4.91–4.98 BM [42]. The presence of four unpaired electrons indicates high-spin Mn^{III} complexes with porphyrins.

3.4. *ESI-mass spectra*

ESI-mass spectra were used for the identity and purity of these Mn^{III}-porphyrins [43–45]. The spectra give m/z 783 for [C$_{50}$H$_{44}$N$_6$Mn − Cl]$^+$, m/z 667 for

$[C_{44}H_{28}N_4Mn]^+$, and m/z 615 for $[C_{44}H_{30}N_4 + H]^+$ for the $[Mn^{III}(TPP)Cl(dah)]$ complex. For the $[Mn^{III}(TPP)Br(dah)]$ complex, m/z 770 for $[C_{44}H_{28}N_4BrMn + Na]^+$, m/z 669 for $[C_{44}H_{28}N_4Mn + 2H]^+$, and m/z 615 for $[C_{44}H_{30}N_4 + H]^+$ were found. For the $[Mn^{III}(TPP)N_3(dah)]$ complex, m/z 727 for $[C_{44}H_{28}N_7Mn + H_2O]^+$, m/z 668 for $[C_{44}H_{28}N_4Mn + H]^+$, m/z 615 for $[C_{44}H_{30}N_4 + H]^+$, and for the $[Mn^{III}(TPP)NCS(dah)]$ complex, m/z 727 for $[C_{45}H_{28}N_5SMn + 2H]^+$, m/z 685 for $[C_{44}H_{28}N_4Mn + H_2O]^+$, and m/z 615 for $[C_{44}H_{30}N_4 + H]^+$ were found.

3.5. *De-polymerization activity*

The Mn^{III}-porphyrin complexes were tested for humic acid de-polymerization activity by measuring absorbance increase at 360 nm and absorbance decrease at 450 nm in solutions containing humic acid and Mn^{III}-porphyrins. The results are shown in figure 1. Out of four Mn^{III}-porphyrins synthesized, three, chloro(tetraphenylporphinato)Mn^{III} (1,6-diaminohexane), bromo(tetraphenylporphinato)Mn^{III}(1,6-diaminohexane), and azido(tetraphenyl-porphinato)Mn^{III}(1,6-diaminohexane), de-polymerize humic acid. However, thiocyanato-(tetraphenylporphinato)Mn^{III}(1,6-diaminohexane) does not
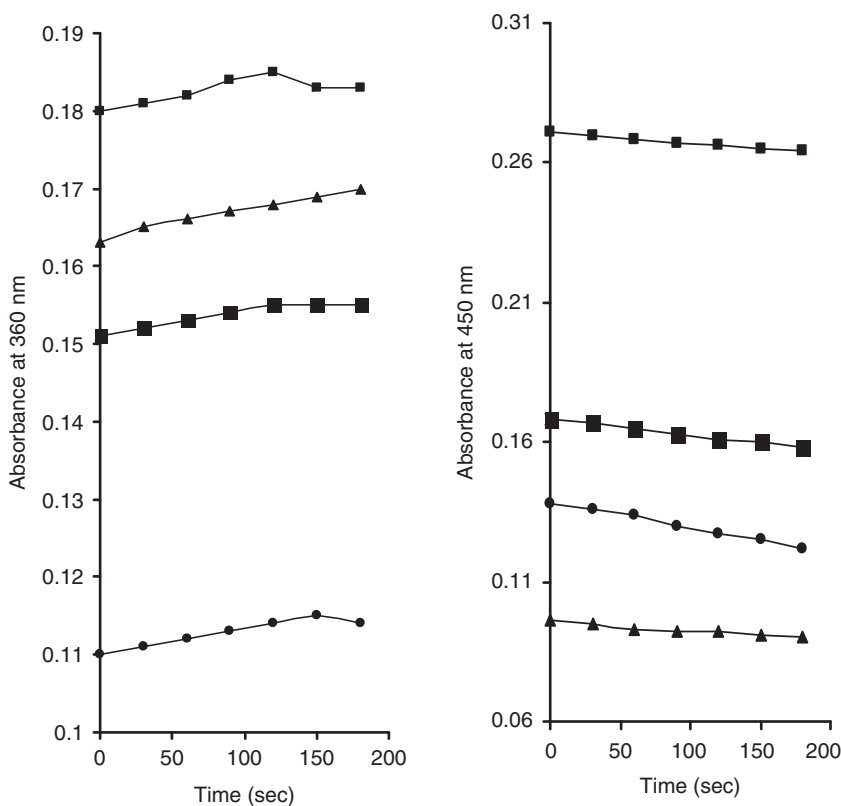

Figure 1. De-polymerization activities toward humic acid, where ▲ = de-polymerization activity of [Mn(TPP)N$_3$(dah)], ● = de-polymerization activity of [Mn(TPP)Cl(dah)], ■ = average curve for de-polymerization activities of Mn^{III}-porphyrins, and ■ = de-polymerization activity of [Mn(TPP)Br(dah)].
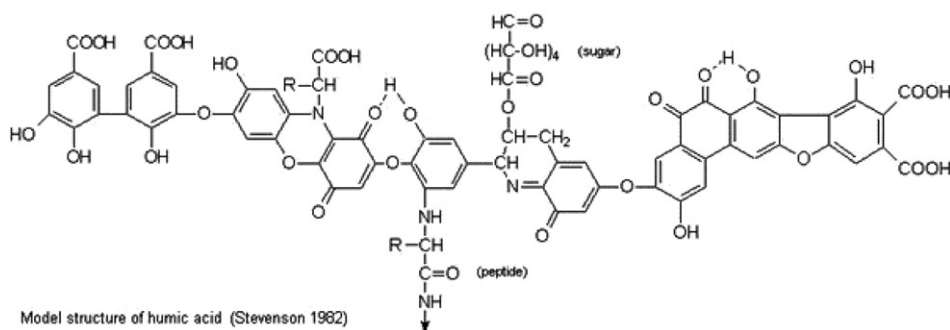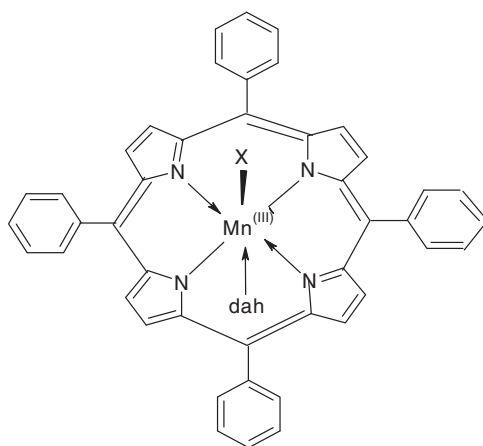
Figure 2.   Structure of humic acid.

Figure 3.   Proposed structure for Mn^{III}-porphyrins, where X = Cl$^-$, Br$^-$, N$_3^-$, or NCS$^-$ and dah = 1,6–diaminohexane.

show de-polymerizing activity, possibly due to the decrease in oxidation potential of Mn^{III} by coordination with thiocyanate. The de-polymerization of humic acid by the three Mn^{III}-porphyrin complexes is important for de-polymerization of coal [46] in low molecular mass fraction so that it can be used as a feedstock for preparation of commodity and rare chemicals. The structure of humic acid is given in figure 2.

4. Conclusion

Based on the positions of the NH$_2$ stretching frequency in the IR spectra of these complexes, it was concluded that 1,6-diaminohexane is coordinated to Mn^{III} unidentate. An octahedral geometry has been proposed for all four complexes (figure 3) [17, 47, 48]. Another notable feature of these Mn^{III}-porphyrins is their de-polymerization activity toward humic acid as a model compound. Thus, these complexes mimic the activity of the Mn-peroxidase enzyme, which also shows the de-polymerization activity [16]. These new Mn^{III}-porphyrins are better in that their de-polymerization activities are independent of

pH and temperature. They can de-polymerize humic acid at room temperature and at any pH, whereas the Mn-peroxidase enzyme is pH and temperature sensitive.

Acknowledgments

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