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COORDINATION COMPOUNDS

Novel Mn(III) Porphyrins and Prospects of Their Application in Catalysis[1]

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Abstract—Four novel Mn(III) porphyrins have been synthesized and characterized by UV-Vis, IR, ESI-mass spectroscopy, elemental analysis, magnetic susceptibility studies, TLC, and conductivity measurements. The tentative structure has been proposed. Depolymerization of coal using the synthesized Mn(III) porphyrins have been demonstrated by the optical density method using humic acid as a model of coal. The synthesized complexes have shown excellent depolymerization activity based on comparative studies. Complexes have been successfully applied for the catalytic oxidation of benzyl alcohol, aniline, benzoin, and benzaldehyde into benzaldehyde, nitrobenzene, benzil, and benzoic acid, respectively, at room temperature and pressure.

Keywords: Mn(III) porphyrins, humic acid, biomimetic catalyst, coal depolymerization, oxidation reaction

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INTRODUCTION

Macrocyclic complexes have received much attention because they are involved in important biological processes, such as photosynthesis, dioxygen transport, in addition to catalytic properties [1, 2] with important industrial applications. The increasing demand for catalyst 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 [3–7]. Due to strong complexing properties and catalytic behavior of metalloporphyrins, these complexes have found numerous applications in chemical analysis [8]. Due to their significant properties, manganese porphyrins are highly useful in biochemical applications [9, 10]. The metalloporphyrins generally mimic the functions of lignin peroxidase in degrading lignin model compounds and shown to be an effective catalyst for pulp bleaching and pulp mill effluent decolourization [11]. Lignin peroxidase, a heme containing enzyme secreted by fungal strains [12–14] which oxidizes Mn(II) to Mn(III) in the presence of H_2O_2. It depolymerizes lignin which is a natural polymer of varying composition containing aryl-propyl unit [15]. Humic acid has structural similarity with lignin and considered as coal model. Lignin peroxidase depolymerizes humic acid [16] and this depolymerization activity is due to the Mn(III) chelated complexes.

Water solubility is another required property for the porphyrins to be utilized in different medicinal purposes, biological and other applications. The study on artificial water soluble porphyrins is currently under active research regarding to design, synthesize and biological assay [17, 18]. In biomimetic work, the preferred system should contain aqueous medium. However, the main drawback of the most of Mn(III) porphyrins are the inadequate solubility in aqueous media. To overcome this limitation, the authors were tried to work on this drawback. On other hand, the effective biomimetic catalytic activity of Mn(III) porphyrins prompted us to explore their depolymerization activity towards humic acid, so that low molecular weight coal fractions can be used as a feed stock for commodity and rare chemicals as an alternative to depleting oil reserves which are at present the basis of our chemical industries. The use of Mn(III) porphyrins as effective catalysts in the oxidation of various organic substrates like benzyl alcohol, aniline, benzoin and benzaldehyde was another significant objective of this work.

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[1] The article is published in the original.

EXPERIMENTAL

Chemicals

All the chemicals which have been used were of A.R. grade and have been purified and dried whenever necessary by the standard methods [19–21]. Pyrrole was purchased from Merck (Germany) and acetylacetone from S.D.-fine chemicals (Mumbai). Pyrrole and acetyleacetone havebeen used 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 has been prepared in Milli-Q water 1 mg/mL while the complexes have been used in 10^{-3} M concentration.

All the chemicals used in the study of catalytic oxidation reaction were obtained from pure grade of SRL MERCK and OTTO. A mild oxidant H_2O_2 was used in all the catalytic oxidation-reactions. The characterizations of products were done by IR spectra (Model) by using KBr disc. The progresses of reactions were monitored by UV-Visible spectroscopy.

Characterization

The complexes were analyzed using standard procedures [22, 23]. The elemental analyses have been done from Cochin University of Science and Technology, Cochin. Electronic spectra were recorded on Hitachi (Japan) model U-2000. I.R. spectra were recorded on 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 century digital conductivity meter; model CC-601 with 10^{-3} M 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 the volume ratio of 1 : 4 as the solvent. Coal depolymerization study was based on previous literature study [15, 16, 24].

Synthesis

H_2TPP (meso-tetraphenylporphyrin) was synthesized by known Adler method [25]. The synthesis of Mn(III) porphyrins was carried out by adopting a combined literature methods [26, 27]. The bis (acetylacetonato)Mn(III) complexes with axial halo- or pseudohalo groups i.e. Cl^-, Br^-, N_3^- or NCS^-, serve as useful synthetic intermediate for the synthesis of Mn(III) porphyrins [28]. The Mn(III) porphyrins were synthesized by our previous literature method [24].

Synthesis of Mn(III) porphyrin with 1,2-diaminoethane, [Mn(TPP)X(dae)]. For the synthesis of thiocyanato(tetraphenylporphinato)MnIII (1,2-diaminoethane) [Mn(TPP)NCS(dae)], 0.725 g (0.001 mole) of [Mn(TPP)NCS], along with 4 mL of 1,2-diaminoethane was stirred for 25 minutes and then refluxed for 36 h. After refluxing the whole content was cooled at room temperature for 1 h then dried under vacuum over P_2O_5. Thus, obtained black crystals were re-crystallized with ethanol. The obtained yield was 0.640 g (81%). The other complexes were prepared in the same way. All these complexes were hygroscopic in nature.

Catalytic Applications

Coal depolymerization activity. The coal depolymerization activity of the Mn(III) porphyrins was recorded on the same spectrophotometer as mentioned above using 1 mL capacity cuvettes at room temperature. The depolymerization activity has been assessed by measuring the decrease in absorbance at 450 nm and increase in absorbance at 360 nm [15, 16, 24]. 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 interval of 30 s at 450 nm and 360 nm respectively.

In other catalytic applications of manganese porphyrins, oxidation of different substrates like benzyl alcohol, aniline, benzoin and benzaldehyde was performed based on literature study [29, 30] and similar methodology was applied successfully to all aforementioned substrates.

Oxidation of benzyl alcohol. In a 50 mL round bottom flask the substrate benzyl alcohol (20 mmol) along with 30% H_2O_2 (2 mmol) was taken in 10 ml of acetonitrile and water in 1 : 1 ratio. The mixture was stirred initially and then, 0.01 mmol of Mn(III) porphyrin as catalyst was added. The whole content was stirred at room temperature for 30 minutes. The progress of reaction was monitored by UV-visible spectroscopy. Excellent yield of benzaldehyde was achieved for each complex that was average 82%.

Oxidation of aniline. In a 50 mL round bottom flask the substrate, aniline (20 mmol) along with 30% H_2O_2 (2 mmol) was taken in 10 mL of acetonitrile solution. The mixture was stirred initially and then 0.01 mmol of Mn(III) porphyrin as catalyst was added. The whole content was stirred at room temperature for 1 hour. The progress of reaction was monitored by using UV-visible spectroscopy. Yield: ~84%.

Oxidation of benzoin. In a 50 mL round bottom flask the substrate benzoin (10 mmol) along with 30% H_2O_2 (2 mmol) was taken in 10 mL of acetonitrile solution. The mixture was stirred initially and then, 0.01 mmol of Mn(III) porphyrin as catalyst was added along with 0.01 mmol of KOH. The whole content was stirred at room temperature for 40 minutes. The progress of reaction was monitored by using UV-visible

Table 1. Physical properties of Mn(III) porphyrins, colour—black

Complexes	μ_{eff} (B.M.)	Molar conductance (Ω^{-1} cm^2 M^{-1})	Yield, %	Analysis found (calculated), %							Formula weight
				C	H	N	S	Br	Cl	Mn	
[Mn(TPP)Cl(dae)]	4.82	14	58	72.3 (72.0)	4.70 (4.69)	11.0 (10.9)	–	–	4.64 (4.29)	7.20 (7.09)	762
[Mn(TPP)Br(dae)]	4.90	26	37	68.3 (67.9)	4.49 (4.25)	10.4 (9.09)	–	9.89 (9.76)	–	6.80 (6.70)	807
[Mn(TPP)N_3(dae)]	4.85	15	59	71.7 (71.0)	4.71 (4.69)	16.3 (15.9)	–	–	–	7.14 (7.10)	769
[Mn(TPP)NCS(dae)]	4.89	18	81	72.7 (72.1)	5.27 (5.15)	11.6 (11.1)	3.81 (3.75)	–	–	6.52 (6.13)	785

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

[Mn(TPP)Cl(dae)]	[Mn(TPP)Br(dae)]	[Mn(TPP)N_3(dae)]	[Mn(TPP)NCS(dae)]	Assignment
424	425	427	425	ν(Mn–N)
1615	1618	1616	1618	$\nu(C{=}C)_{py}$
1324	1325	1325	1328	$\nu(C{=}N)_{py}$
1176	1175	1178	1175	$\nu(CPN)_{py}$
1560	1560	1555	1560	$\nu(C{=}C)_{ph}$
3021	3020	3022	3020	$\nu(C{-}H)_{ph}$
–	–	–	2080	ν(NCS)
–	–	2023	–	$\nu(N_3)$
3310	3315	3312	3310	$\nu(NH_2)_{\mathrm{coordinated}}$
3421	3422	3422	3422	$\nu(NH_2)_{\mathrm{uncoordinated}}$

spectroscopy. A change in colour was observed during reaction progress. Formation of yellow colour precipitate of benzoin was started. After completion of reaction, yellow precipitate was filtered and dried. Recrystallization was done with ethanol. Yield: ~90%; mp 94–96°C.

Oxidation of benzaldehyde. In a 50 mL round bottom flask the substrate benzaldehyde (20 mmol) along with 30% H_2O_2 (2 mmol) was taken in 10 mL of acetonitrile solution and 0.01 g of ammonium acetate was also added as co-catalyst. The mixture was stirred initially and then 0.01 mmol of Mn(III) porphyrin as catalyst was added. The whole content was stirred at room temperature for 3 hrs. The progress of reaction was further monitored by UV-visible spectroscopy. After completion of reaction, product was filtered, dried and then re-crystallized with hot water. Yield: ~81%, mp 120–123°C.

RESULTS AND DISCUSSION

These [Mn(TPP)X] complexes were dissolved in ethanol and refluxed with 1,2-diaminoethane to give [Mn(TPP)X(dae)]. The proposed reaction scheme may be given as below:

$$\begin{tikzcd}
{[\mathrm{Mn(TPP)X}] + \mathrm{dae}} \arrow[d, "\mathrm{EtOH}"', "26\text{–}36\ \mathrm{h}"] \\
{[\mathrm{Mn(TPP)X(dae)}]}
\end{tikzcd}$$

Where dae = 1,2-diaminoethane

X = Cl^-, Br^-, N_3^- or NCS^-.

All these complexes were soluble in ethanol, methanol, pyridine, chloroform, DMSO, DMF and partially soluble in water (~50%). The molar conductance values of these complexes in ethanol with 10^{-3} M concentration are in the range of 14–26 Ω^{-1} cm^2 mol^{-1}, indicating their non-electrolytic nature [31]. Physical properties of these complexes have been given in Table 1.

All complexes were characterized by IR, electronic, and ESI-mass spectra and their spectral details confirmed the chemical structure of the complexes synthesized. IR spectra details were in good agreement with reported literature for specified bands [32–38]. Selected vibrational frequencies (cm^{-1}) in IR spectra

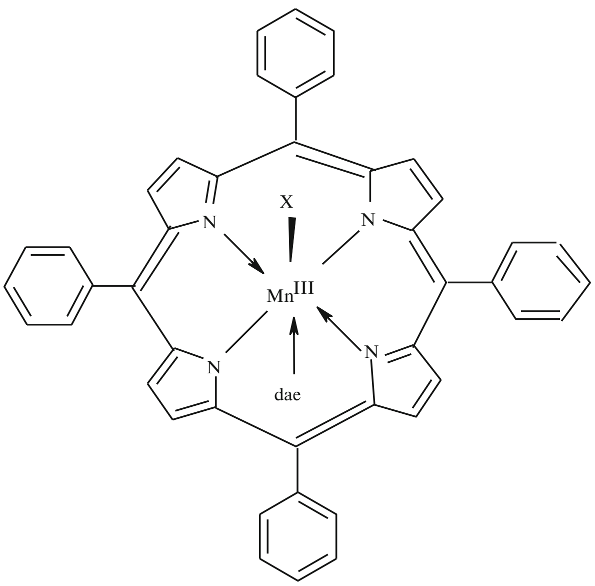

Fig. 1. Proposed chemical structure of Mn(III) porphyrins, where X = Cl^-, Br^-, N_3^- or NCS^-; dae = 1,2-diaminoethane.

of Mn(III) porphyrins are given in Table 2. UV-Visible spectroscopic data for Cl^-, Br^-, N_3^- and NCS^- complexes of manganese(III) porphyrin has been given in Table 3. The assignment of B band has been done on the basis of previous studies [39, 40]. All the data observed for the synthesized Mn^{III}-complexes with H_2TPP and 1,2-diaminoethane were in good agreement with previous literature values. The intense band in the range 460–471 nm in the spectra of these complexes assigned to the charge transfer from a_{1u} and a_{2u} orbitals of porphyrin to $e_g(d\pi)$ orbital of manganese. This respective band in the spectrum is called charge-transfer band [41–43]. The ligand field parameters i.e. $10D_q$, B and β has also been calculated for these Mn^{III}-porphyrins. $10D_q$ have been calculated from the energy of λ_{max} at maximum absorbance. The value of B has been calculated by using the formula D_q/B = 2.7 using Tanabe–Sugano diagram while β has been calculated using formula:

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

The values of B have been found below the free ion value for Mn^{III} ion (1140 cm^{-1}) [44], which indicates covalent metal ligand bonds in all these complexes, with the covalency factor β varying in the range 0.74–0.77 (Table 4).

ESI-mass spectra was used for identity and purity of these Mn(III) porphyrins [7, 45–47]. Different molecular ions obtained for the four Mn(III) porphyrins along with their *m/z* values fully justified the synthesized complexes which are as follow. [Mn(TPP)Cl(dae)] = *m/z* 763 for $[C_{46}H_{36}N_6MnCl]^+$, *m/z* 727 for $[C_{46}H_{36}N_6Mn]^+$, *m/z* 668 for $[C_{44}H_{28}N_4Mn + H]^+$; *m/z* 614 for $[C_{44}H_{28}N_4 + 2H]^+$, [Mn(TPP)Br(dae)] = *m/z* 748 calculated for $[C_{44}H_{28}N_4BrMn + H]^+$; *m/z* 667 for $[C_{44}H_{28}N_4Mn]^+$; *m/z* 614 for $[C_{44}H_{28}N_4 + 2H]^+$, [Mn(TPP)N_3(dae)] = *m/z* 731 calculated for $[C_{44}H_{28}N_7Mn + Na]^+$; *m/z* 667 for $[C_{44}H_{28}N_4Mn]^+$; *m/z* 614 for $[C_{44}H_{28}N_4 + 2H]^+$ and [Mn(TPP)NCS(dae)] = *m/z* 748 calculated for $[C_{45}H_{28}N_5SMn + Na]^+$; *m/z* 668 for $[C_{44}H_{28}N_4Mn + H]^+$; *m/z* 614 for $[C_{44}H_{28}N_4 + 2H]^+$.

The magnetic susceptibility measurements show that these complexes have μ_{eff} values in the range of 4.82–4.90 B.M. [48]. The presence of four unpaired electrons indicates the high spin Mn(III) complexes with porphyrins.

On the basis of aforementioned characterization measurements, all the four complexes have been proposed to be a hepta-coordination complex with axial ligands in transposition (Fig. 1).

Catalytic Applications

All these newly synthesized Mn(III) porphyrins were tested for their coal depolymerization activity towards humic acid for their coal depolymerization activity towards humic acid by measuring absorbance decrease at 450 nm and absorbance increase at 360 nm in solution containing humic acid and Mn(III) porphyrins. The results of the studies have been given in Fig. 2. Figure 2a shows the depolymerization of dark

Table 3. UV-visible spectroscopic data of free base porphyrin and Mn(III) porphyrins

Ligand/Complexes	λ_{max}, nm	
	B(soret) band	Q band
H_2TPP	406	635
[Mn(TPP)Cl(dae)]	460	647
[Mn(TPP)Br(dae)]	462	655
[Mn(TPP)N_3(dae)]	475	661
Mn(TPP)NCS(dae)	471	675

Table 4. Ligand field parameters calculated for Mn(III) porphyrins

Complexes	$10D_q$, cm^{-1}	B, cm^{-1}	β
[Mn(TPP)Cl(dae)]	23764	880	0.77
[Mn(TPP)Br(dae)]	23148	851	0.75
[Mn(TPP)N_3(dae)]	23062	854	0.74
[Mn(TPP)NCS(dae)]	22893	847	0.74

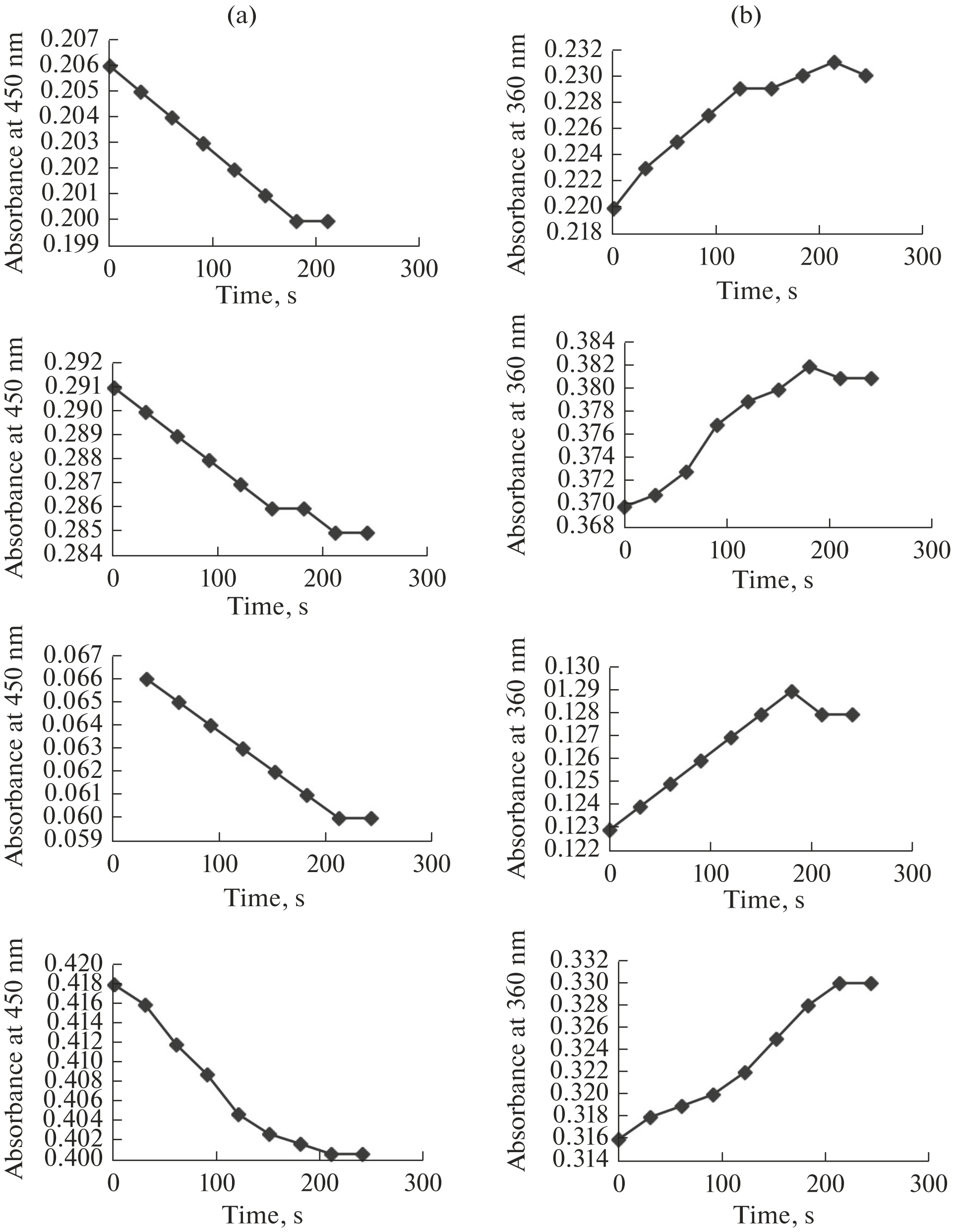

Fig. 2. (a) Depolymerization activity of [Mn(TPP)Cl(dae)], Mn(TPP)Br(dae)], [Mn (TPP)N_3(dae)] and [Mn(TPP)NCS(dae)], respectively at 450 nm. (b) Depolymerization activity of [Mn(TPP)Cl(dae)], [Mn(TPP)Br(dae)], [Mn (TPP)N_3(dae)] and [Mn(TPP)NCS(dae)] respectively at 360 nm.

brown humic acid (decrease in absorbance at 450 nm) and Fig. 2b shows the formation of yellowish coloured compounds (increase in absorbance at 360 nm). Thus, it has been shown that all these Mn(III) porphyrins depolymerize the high molecular mass coal fraction into smaller ones. Our all the synthesized porphyrins have good levels of water solubility in comparing to our previously reported Mn(III) complexes and thus, showed the excellent depoymerization activity in compare to our previously reported porphyrin complexes [24] which is clear from Fig. 2. The mechanism of breakdown is still to be investigated.

In other catalytic applications; conversion of benzyl alcohol into benzaldehyde, aniline into nitrobenzene, benzoin into benzyl and benzaldehyde into benzoic acid have been performed by using manganese porphyrin complexes (Table 5). In a case of conversion of benzyl alcohol to benzaldehyde, the progress of reaction was monitored by taking UV-visible spectra at every 10 minutes of interval. In the spectra, from the beginning and at the end of reaction, a hypochromic shift of the Mn(III)porphyrin Soret bands with small loss of intensity has been observed. A characteristic IR band appeared at 1674 cm^{-1} for C=O stretching fre-

Table 5. Catalytic applications of synthesized manganese porphyrin complexes in conversion reactions

S. No.	Reactants	Products	Temperature	Reaction time, min	Yields, %
1	Benzyl alcohol	Benzaldehyde	Room	30	~82
2	Aniline	Nitrobenzene	Room	60	~84
3	Benzoin	Benzil	Room	40	~90
4	Benzaldehyde	Benzoic acid	Room	180	~81

quency. A small peak at 3075 cm^{-1} for aromatic C—H group while a medium peak at 2730 cm^{-1} for aldehydic C—H group was found. In a case of conversion of aniline to nitrobenzene, the progress of the reaction was monitored by UV-visible spectra taken at every 15 min interval. With the progress of reaction, the intensity of Soret band of the manganese porphyrin catalyst was increased and also shifted towards lower wavelength. In IR spectra of product, the more prominent peak at 1516 cm^{-1} for asymmetric stretching and a medium peak at 1360 cm^{-1} for symmetric stretching of N—O bond of nitro group appeared. Similarly, spectral results and usual laboratory tests were also complied with benzil and benzoic acid formation from benzoin and benzaldehyde respectively.

CONCLUSIONS

In present study, we have synthesized novel Mn(III) porphyrins which show excellent coal depolymerization performance for humic acid, a lignin model compound. Thus, these complexes mimic the activity of lignin peroxidase enzyme, which also shows the de-polymerization activity but the notable and important difference is that these complexes show their activity at room temperature at any pH whereas lignin peroxidase is pH and temperature sensitive. Easy preparation, short reaction time, independent of particular pH and temperature make this an effective useful method for the de-polymerization of coal and other lignin model compounds. Such complexes have also been used to analyze their ability to catalyze the oxidation reactions. The milder reaction condition, room temperature and pressure, less time requirement of reaction, high reactivity and selectivity make these catalysts efficient for the oxidation reactions.

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REFERENCES

1. P. Souza, M. A. Mandiola, A. Arquero, et al., Naturforsch. Z. B **49**, 263 (1994).
2. N. R. Champness, C. S. Frampton, G. Reid, et al., J. Chem. Soc. Dalton Trans., 3031 (1994). doi 10.1039/DT9940003031
3. J. T. Groves, J. Porphyrins Phthalocyanines, **4**, 350 (2000). doi
4. S. Nimri and E. Keinan, J. Am. Chem. Soc. **121**, 8978 (1999). doi 10.1021/ja990314q
5. M. V. Vinodu and M. Padmanabhan, Proc. Indian Acad. Sci. (Chem. Sci.) **113**, 1 (2001).
6. M. M. Q. Simos, M. G. P. M. S. Neves, and J. A. S. Cavaleiro, Jord. J. Chem. **1**, 1 (2006).
7. I. Batinic-Haberle, I. Spasojevic, R. D. Stevens et al., Dalton Trans., 617 (2006). doi 10.1039/B513761F
8. M. Biesaga, K. Pyrzynska, M. Trojanowicz, Talanta, **51**, 209 (2000). doi 10.1016/S0039-9140(99)00291-X
9. L. F. Lauffer, Chem. Rev. **87**, 901 (1987). doi 10.1021/cr00081a003
10. M. Ravikanth and T. K. Chandrashekhar, Structure-Bond. **82**, 105 (1995). doi 10.1007/BFb0036827
11. *Biotechnology in Pulp and Paper Industry*, Eds. by P. S. Skerker, R. L. Farrell, D. Dolphin, F. Cui, and T. Wijesekera (Butterworth-Heinemann, Boston, 1990), Ch. 18.
12. D. L. Crawfold and R. L. Crawfold, Enz. Microb. Technol. **2**, 11 (1980). doi 10.1016/0141-0229(80)90003-4
13. S. B. Pointing, A. L. Pelling, G. J. D. Smith, et al., Mycol Res. **109**, 115 (2005). doi 10.1017/S0953756204001376
14. V. Shanmugam and K. D. S. Yadav, Indian J. Exp. Biol. **34**, 116 (1996).
15. M. Hofrichter, Enz. Microbiol. Technol. **30**, 454 (2002). doi 10.1016/S0141-0229(01)00528-2
16. M. Yadav, P. Yadav, K. D. S. Yadav, Biochemistry (Moscow) **74**, 1125 (2009). doi 10.1134/S0006297909100083
17. T. Murashima, S. Tsujimoto, T. Yamada, et al., Tetrahed. Lett. **46**, 113 (2005). doi 10.1016/j.tetlet.2004.11.024
18. J. M. Pedrosa, M. Perez, I. Prieto, Phys. Chem. Chem. Phys. **4**, 2329 (2002). doi 10.1039/B108360K
19. R. J. Errington, *Advanced Practical Inorganic and Metalloorganic Chemistry*, 1st Ed. (Chapman and Hall, London, 1997).
20. W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th Ed. (Butterworth-Heinemann, Oxford, 1997).

21. B. S. Furniss, A. J. Hannaford, V. Rogers, et al., *Vogel's Text Book of Practical Organic Chemistry*, 4th Ed. (ELBS, London, 1984).
22. G. H. Jeffery, J. Bassett, J. Mendham, et al., *Vogel's Text Book of Quantitative Chemical Analysis*, 5th Ed. (ELBS, London, 1996).
23. S. Yadava and S. L. Bharati, J. Coord. Chem. **64**, 3950 (2011). doi .10.1080/958972.2011.632412
24. S. L. Bharati and S. Yadava, J. Coord. Chem. **65**, 3492 (2012). doi .10.1080/00958972.2012.718763
25. A. D. Adler, F. R. Longo, J. D. Finarelli, et al., J. Org. Chem. **32**, 476 (1967). doi 10.1021/jo01288a053
26. E. B. Fleischer, J. M. Palmer, T. S. Srivastava, et al., J. Am. Chem. Soc. **93**, 3162 (1971). doi 10.1021/ja00742a012
27. B. R. Stults, V. W. Day, E. L. Tassett, et al., Inorg. Nucl. Chem. Lett. **9**, 1259 (1973). doi 10.1016/0020-1650(73)80007-8
28. B. R. Stults, V. W. Day, R. S. Marianelli, and V. B. Day, Inorg. Chem. **14**, 722 (1975). doi 10.1021/ic50146a004
29. B. Bahramian, V. Mirkhani, M. Moghadam, et al., Appl. Catal. A: Gen. **315**, 52 (2006). doi 10.1016/j.apcata.2006.08.037
30. S. L. H. Rebelo, M. M. Q Simoes, M. G. P. M. S. Neves, et al., J. Mol. Catal. A: Chem., **201**, 9 (2003). doi 10.1016/S1381-1169(03)00149-3
31. S. F. A. Kettle, *Coordination Compounds* (Pitman Press, London, 1975)
32. D. W. Thomas and A. E. Martell, J. Am. Chem. Soc. **78**, 1338 (1956). doi 10.1021/ja01588a021
33. R. J. H. Clark and C. S. Williams, Spectrochim. Acta **22**, 1081 (1966). doi 10.1016/0371-1951(66)80198-4
34. R. J. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds* (Prentice-Hall of India, New Delhi, 1969).
35. T. N. Lomova and B. D. Berezin, Russ. J. Coord. Chem. **27**, 85 (2001). doi 10.1023/A:1009523115380
36. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, *Comprehensive Coordination Chemistry* (Pergamon, Oxford, 1987).
37. I. Gamo, Bull. Chem. Soc. Jpn. **34**, 760 (1961). doi 10.1246/bcsj.34.760
38. A. D. Allen and C. V. Senoff, Canad. J. Chem. **43**, 888 (1965). doi 10.1139/v65-115
39. J. W. Buchler, W. Kokisch, and P. Smith, Struct. Bond. (Berlin) **34**, 79 (1978).
40. H. Sckeno and H. Kobayashi, J. Chem. Phys. **75,** 283 (1981).
41. E. Fagadar-Cosma, M. C. Mirica, I. Balcu, et al., Molecules **14**, 1370 (2009). doi 10.3390/molecules14041370
42. Y. Lamamoto, M. D. Assis, K. J. Ciuffi, et al., J. Mol. Catal. A: Chem. **116**, 365 (1997). doi 10.1016/S1381-1169(96)00343-3
43. H. A. O. Hill, A. J. Macfarlane, and R. J. P. Williams, J. Chem. Soc. A, **1704** (1969). doi 10.1039/J19690001704
44. J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry, Principles of Structure and Reactivity* (Pearson, Singapore, 2005), p.445.
45. S. L. Bharati, P. K. Chaurasia, and S. Yadava, J. Coord. Chem. **61**, 232 (2016). doi 10.1134/S0036023616020212
46. I. Batinic-Haberle, I. Spasojevic, R. D. Stevens, et al., J. Chem. Soc. Dalton Trans., 2689 (2002). doi 10.1039/B201057G
47. I. Batinic-Haberle, I. Spasojevic, R. D. Stevens, et al., Dalton Trans., 1696 (2004). doi 10.1039/B400818A
48. D. V. Behere and S. Mitra, Inorg. Chem. **19**, 992 (1980). doi 10.1021/ic50206a039