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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis of a Novel Manganese(III) Porphyrin and Its Catalytic Role in Selective Oxidation of Aromatic Alcohols

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Abstract—A novel azido complex of manganese(III) porphyrin with 1-methylimidazole has been synthesized. This complex can be abbreviated as $[Mn^{III}(THMPP)N_3(1\text{-}MeIm)]$, where THMPP is 5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphine and 1-MeIm is1-methylimidazole. The complex has been characterized by UV-visible, FT-IR, ESI-MS spectra, elemental analysis, and magnetic susceptibility. The tentative structure has been proposed to be octahedral. The catalytic activity of the complex synthesized has been studied using different oxidants in the selective oxidation of aromatic alcohols to aldehydes. The selectively transformed products have been obtained under room conditions and short time period in high yields.

Keywords: manganese(III) porphyrin, 1-methylimidazole, 5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphine, alcohol, catalyst, oxidation

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In recent years, interest for the synthesis of manganese porphyrins due to their applications in biomimetic chemistry and oxidation catalysis is rapidly increased. Synthetic manganese porphyrins can mimic the actions of superoxide dismutase (SOD) [1–3] and catalase enzymes [4–7]. These are extensively used as structural and functional models of the cytochrome P-450, a well known monooxygenase enzyme [8, 9].

Transformation of organic substrates into their useful forms is extremely beneficial for the large scale production. The classical oxidation methods generally take long time for completion of reactions with low selectivity and produce immense amounts of hazardous wastes. To overcome these drawbacks, various transition metal based catalysts are being used. Metalloporphyrin is the most important class of catalysts which is being used in such types of oxidation reactions. *Meso*-tetraarylporphyrin derivatives generally show better catalytic activities among all the synthetic porphyrins. The first use of synthetic metalloporphyrin as a catalyst in the oxidation reactions was reported by Groves and coworkers in 1979 [10]. After then, many researchers have attempted to use metalloporphyrins as catalysts in various organic syntheses [11–29].

In this work, a novel manganese(III) porphyrin complex has been synthesized and characterized. The catalytic properties have also been tested in the oxidation of aromatic alcohols to their corresponding aldehydes using different oxidants.

EXPERIMENTAL

Materials

4-Hydroxy-3-methoxybenzaldehyde (Vanillin), benzyl alcohol, sodium periodate and hydrogen peroxide were purchased from S.D. Fine-Chem Limited (Mumbai). 1-Methylimidazole and 4-methoxybenzyl alcohol were purchased from Chemical Centre (Mumbai). Sodium hypochlorite was purchased from Merck (Mumbai). Chemicals were of A.R. grade. Pyrrole (Merck, Germany) and acetylacetone (S.D. Fine-Chem Limited, Mumbai) were freshly distilled before use. Milli-Q water has been used during the experiment from our laboratory (Waters Millipore).

Physical Measurements

Electronic spectra were recorded in methanol on a Hitachi (Japan) spectrophotometer model U-2900 from 190–900 nm in our laboratory. FT-IR spectra were recorded on a Perkin Elmer spectrum II spectrophotometer using potassium bromide pellets (4000–400 cm^{-1}). ESI-Mass spectra were recorded on a

Waters UPLC-TQD device. FT-IR and ESI-Mass data were provided by SAIF, CDRI (Central Drug Research Institute, Lucknow). Electrical conductivity data were recorded on a TOSHCON Auto ranging Conductivity Meter TCM 15+ by preparing 10^{-3} molar solution in ethanol at room temperature. Elemental analyses were carried out on an Elemental Vario EL III by SAIF, STIC (Cochin). Magnetic susceptibility measurements were obtained at room temperature on a Vibrating Sample Magnetometer from IIT (Kanpur).

Synthesis of Complexes

Preparation of porphyrin [H_2THMPP]. The porphyrin ligand, i.e. 5,10,15,20-tetra(4-hydroxy-3-methoxyphenyl) porphine [H_2THMPP], was synthesized by using Adler's method with some modifications [30]. In this method, 5.6 mL (0.08 mol) of freshly distilled pyrrole and 12.16 g (0.08 mol) of vanillin were added in 300 mL of boiling propionic acid and the whole reaction mixture was refluxed for 2 h. After cooling, the reaction mixture was kept in refrigerator for 12 h. The reaction mixture was filtered and washed thoroughly with methanol until the filtrate became colorless. The purple color crystals of porphyrin were recrystallized with 1 : 1 ratio of chloroform and dichloromethane.

Preparation of azide complex of manganese(III) porphyrin [Mn^{III}(THMPP)N_3]. First of all, $Mn^{III}(acac)_2N_3$ (where acac = acetylacetonate) has been synthesized by using literature method [31]. This acetylacetonate complex of manganese(III) act as intermediate in the preparation of manganese(III) porphyrin complex [32–34]. Preparation of Mn^{III}(THMPP)N_3 was done by taking 0.003 mol of $Mn^{III}(acac)_2N_3$ and H_2THMPP and dissolved it in 150 mL of glacial acetic acid containing 45 mL acetic anhydride. The whole reaction mixture was refluxed for 4 h. After removing the solvent by evaporation on steam-bath, bluish-green crystalline solid complex was obtained. Recrystallization was done with 1 : 1 ratio of chloroform and methanol.

Preparation of manganese(III) porphyrin complex with 1-methylimidazole [Mn^{III}(THMPP)N_3(1-MeIm)]. 01 mmol (0.90 g) of Mn^{III}(THMPP)(N_3) was dissolved into 8 mL of methyl alcohol with further addition of 1-methylimidazole (10 mmol, 0.8 mL) to it followed by stirring for about 10 minutes. It was refluxed for 23 h and cooled at room temperature for 1 h. The reaction mixture was filtered and filtrate has been evaporated and dried under vacuum over P_2O_5. After drying, complex was found as blackish-green coloured sticky solid. Yield – 0.78 g (80.41%).

For $C_{52}H_{42}N_9O_8Mn$ anal. calcd. (%): C, 64.00; H, 4.34; N, 12.92; O, 13.12; Mn, 5.63.

Found (%): C, 64.11; H, 4.37; N, 12.84; O, 13.08; Mn, 5.60.

Catalytic Applications

Oxidation of alcohol to aldehyde catalyzed by Mn(THMPP)N_3(1-MeIm). Catalytic application was based on the literature studies [35–38]. 2 mmol of aqueous oxidant sodium periodate was added to the solution of acetonitrile (5 mL), alcohol (0.5 mL), and complex (0.01 g). Now, solution was stirred using magnetic stirrer at room temperature. 1 mL aliquots of the reaction mixture were withdrawn at regular intervals of 5 min and UV-visible spectra were recorded using UV-visible spectrophotometer Hitachi (Japan) model U-2900.

RESULTS AND DISCUSSION

Characterization of the Complex

The newly synthesized manganese(III) complex was hygroscopic and blackish-green in colour. It was soluble in methyl alcohol, ethyl alcohol, acetone, acetonitrile and chloroform. The molar conductance (11 Ω^{-1} cm^2 mol^{-1}) indicates its non-electrolytic character [39].

UV-visible spectral studies. The UV-visible spectrum of Mn^{III}(THMPP)N_3 exhibits a strong B band at 415 nm and four Q bands at 510, 545, 585 and 640 nm [40–42]. In case of Mn^{III}(THMPP)N_3(1-MeIm), two Q bands disappeared in the spectrum due to the coordination of sixth ligand. There was red shift in B band (470 nm) and blue shift in Q bands (570, 605 nm).

The calculated values of ligand field parameters i.e. 10Dq, B, and β for Mn^{III}(THMPP)N_3(1-MeIm) were 23585 cm^{-1}, 873 cm^{-1}, and 0.77 respectively. The crystal field splitting energy (10Dq) has been calculated with the help of λ_{max} value at maximum absorbance. Tanabe-Sugano diagram has been used for calculating Racah interelectronic repulsion parameter (B) whereas covalency factor (β) has been calculated with following formula:

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

where $B_{\text{free ion}}$ for Mn^{3+} ion = 1140 cm^{-1} [43]; β is less than 1, which means that the B value of complex is below the free ion value and thus confirms that the metal-ligand bond in the newly synthesized complex is covalent in nature.

FT-IR spectral studies. The significant peaks observed in the FT-IR spectrum of Mn(THMPP)N_3(1-MeIm) are given in Table 1. These peaks indicate the formation of the novel complex.

Magnetic susceptibility measurements. Magnetic moment is calculated with the help of magnetic susceptibility [44]. The μ_{eff} value for the complex was 4.78

Table 1. Selected vibrational frequencies (cm^{-1}) in FT-IR spectrum of Mn(THMPP)N_3(1-MeIm)

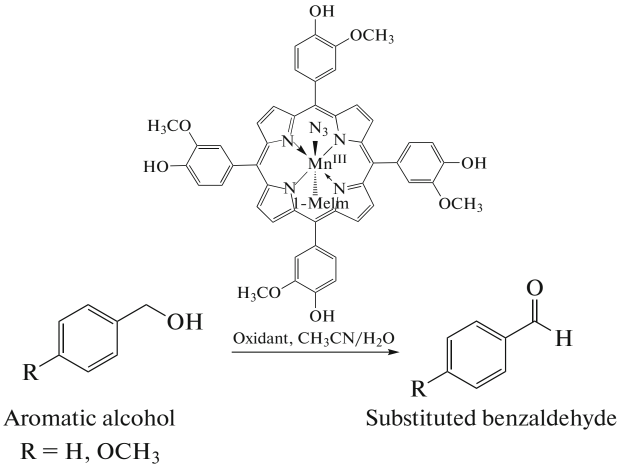
ν, cm^{-1}	Assignment
621	Ring torsion (1-MeIm)
662	OPP bend (1-MeIm)
763	C–Hbend (pyrrolic)
1090	C–Hrock (pyrrolic)
1168	OCH_3
1204	C–N str
1273	N_3
1414	C=N (pyrrolic)
1456	C–H bend (OCH_3)
1519	In plane str (1-MeIm)
1590	C=C (ph)
2859	C–Hstr
3115	C–Hstr (aromatic ring of 1-MeIm)
3437	O–H

which indicate the presence of four unpaired electrons and confirms the formation of high-spin manganese(III) complex [45–47].

ESI-Mass spectral studies. The ESI-MS spectrum of Mn(THMPP)N_3(1-MeIm) shows m/z values at 811, 852, 853, 854, 934, 935, 936 and 950 which correspond to $[C_{48}H_{36}N_5O_8]^+$, $[C_{48}H_{36}N_4O_8Mn]^+$, $[C_{48}H_{36}N_4O_8Mn + H]^+$, $[C_{48}H_{36}N_4O_8Mn + 2H]^+$, $[C_{52}H_{42}N_6O_8Mn]^+$, $[C_{52}H_{42}N_6O_8Mn + H]^+$, $[C_{52}H_{42}N_6O_8Mn + 2H]^+$ and $[C_{52}H_{42}N_7O_8Mn+ 2H]^+$ ions respectively. These ions indicate the constituent fragments of the molecule and thus help in the structure elucidation.

Catalytic Properties

The utility of the novel azido complex of manganese(III) porphyrin with 1-methylimidazole as a catalyst in the oxidative conversion of benzyl alcohol to benzaldehyde and 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde has been tested (Scheme 1). In these experiments, $NaIO_4$, H_2O_2 and NaOCl have been used as oxygen source. The product characterization has been done by UV-visible, TLC and qualitative analysis. The percentage yields of the products obtained have been given in Table 2. Blank experiments have also been done which gave only trace amount of products. There are some other papers of manganese based catalytic application may be helpful for readers [48–54].



Scheme 1. Oxidation of alcohols to aldehydes catalyzed by Mn(THMPP)N_3(1-MeIm).

CONCLUSIONS

A new manganese(III) porphyrin complex with 1-methylimidazole has been synthesized and characterized. The catalytic activity of this complex has also been tested in selective oxidative transformation of alcohols to aldehydes. Benzyl alcohol and 4-methoxybenzyl alcohol for the oxidation reactions were selected as substrate while $NaIO_4$, H_2O_2 and NaOCl have been used as oxygen source. These reactions take place at room temperature and complete in 20 min only.

Table 2. Product yields in oxidation of benzyl alcohol catalyzed by Mn(THMPP)N_3(1-MeIm) with different oxidants

Entry	Substrate	Oxidant	Solvent	Product yield (%) after 20 min
1	Benzyl alcohol	$NaIO_4$	CH_3CN/H_2O	86
2	Benzyl alcohol	H_2O_2	CH_3CN	69
3	Benzyl alcohol	NaOCl	CH_3CN	34
4	4-Methoxybenzyl alcohol	$NaIO_4$	CH_3CN/H_2O	90
5	4-Methoxybenzyl alcohol	H_2O_2	CH_3CN	76
6	4-Methoxybenzyl alcohol	NaOCl	CH_3CN	38

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SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at https://doi.org/10.1134/S003602361909002X and are accessible for authorized users. Supporting information includes UV-visible, FT-IR, ESI-MS spectra, and magnetic susceptibility graph of Mn(THMPP)N3(1-MeIm).

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