

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:29

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Novel complexes of Mn(III) with macrocyclic porphine ligand and ethylenediamine

Sudha Yadava^a & Shashi Lata Bharati^a

^a Department of Chemistry, DDU Gorakhpur University, Gorakhpur-273009, India

Published online: 14 Nov 2011.

To cite this article: Sudha Yadava & Shashi Lata Bharati (2011) Novel complexes of Mn(III) with macrocyclic porphine ligand and ethylenediamine, *Journal of Coordination Chemistry*, 64:22, 3950-3959, DOI: [10.1080/00958972.2011.632412](https://doi.org/10.1080/00958972.2011.632412)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.632412>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Novel complexes of Mn(III) with macrocyclic porphine ligand and ethylenediamine

SUDHA YADAVA* and SHASHI LATA BHARATI

Department of Chemistry, DDU Gorakhpur University, Gorakhpur-273009, India

(Received 26 October 2010; in final form 29 September 2011)

The present work describes the synthesis and characterization of a few Mn(III) porphyrins with ethylenediamine. A new series of high-spin Mn(III) porphyrins having general formula [Mn(TMPP)X] and [Mn(TMPP)X(en)], where TMPP = tetra-*p*-methoxyphenylporphinate ligand, X = Cl⁻, Br⁻, N₃⁻ or NCS⁻ and en = ethylenediamine. Molar conductance values of these complexes show their non-electrolytes in ethyl alcohol. These complexes have been characterized by U.V., I.R., ESI-mass spectra, elemental analyses and magnetic susceptibility measurements. The tentative structures have also been proposed.

Keywords: Tetra-*p*-methoxyphenylporphine; Ethylenediamine; Mn(III) porphyrins; Spectroscopic studies

1. Introduction

Macrocyclic complexes have received much attention [1] because they are involved in important biological processes, such as photosynthesis and dioxygen transport, in addition to catalytic properties [2] with important industrial applications. Their enhanced kinetic and thermodynamic stabilities led to potential applications as metal extrants [3], radiotherapeutic [4] and medical imaging agents [5]. The occurrence of the porphyrin rings in nature in such crucial and multiple roles as those spanned by the heme-proteins, chlorophyll and vitamin B₁₂ suggest that advantages are associated with this macrocyclic structure [6]. The coordination of anions and small or large molecules to metalloporphyrins determines their role in enzymatic and catalytic reactions [7, 8]. In metalloporphyrins, electron transfer reactions can be finely tuned by the metal, the porphyrin macrocycle and the electronic properties of the axial ligands [9]. There has been growing interest [9, 10] in manganese porphyrins because of their reactivity and accessibility of several oxidation states that can be used for redox cycles useful for biochemical applications.

Mn(III) porphyrins have been used as catalysts in oxidative degradation of plasmid bluescript [11] and as ionophores in potentiometric, piezoelectric or fluorimetric sensor devices for detection of hydrazine [12], thiocyanate [13], dioxins [14] and salicylate [15]. Mn(III) porphyrins using tetraphenylporphines have been studied extensively [16–19].

*Corresponding author. Email: dr_sudhayadava@yahoo.co.in

We have chosen tetra-p-methoxyphenylporphine to see changes in the properties of Mn(III) porphyrin complexes with the objective of finding better Mn(III) porphyrin complexes for the applications mentioned above.

2. Experimental

2.1. Materials

All chemicals were of A.R. grade and have been purified and dried whenever necessary by the standard methods as given in literature [20–22]. Pyrrole (Merck, Germany) and acetylacetonone (S.D.-fine chemicals, Mumbai), have been freshly distilled prior to use. Milli-Q water has been used throughout the experimental procedures.

2.2. Physical measurements

The complexes were analyzed using standard procedures [23]. C, H, and N contents were analyzed from Cochin University of Science and Technology, Cochin. Conductivity measurements were carried out on a Century digital conductivity meter, model CC-601, with 10^{-3} mol L⁻¹ concentration in ethanol at room temperature. Purity of the complexes was checked by TLC plates using silica gel adsorbent and CH₂Cl₂/CH₃OH in 8/2 ratio. Electronic spectra were recorded on a Hitachi (Japan) model U-2000 from 200–1100 nm in methanol. IR spectra were recorded using KBr discs on a Perkin-Elmer (model-557) Beckman Acculab-10. Magnetic susceptibility measurements were carried out at room temperature using a EV7VSM (ADE-DMS, USA) Vibrating Sample Magnetometer, from IIT, Kanpur. ESI-mass spectra were recorded on a WATERS-Q-T of Premier-HAB213 using ethanol as solvent, from IIT, Kanpur.

2.3. Syntheses

2.3.1. Preparation of ligand. Tetra-p-methoxyphenylporphine has been synthesized by literature method [24]. Freshly distilled pyrrole 5.6 mL (0.08 mol) and 9.7 mL (0.08 mol) of anisaldehyde were refluxed with 300 mL of propionic acid for 30 min. The solution was cooled at room temperature and filtered. Dark shining purple crystals were obtained, washed with methanol, followed by hot water and finally dried in vacuum. Recrystallization was done with 1 : 1 ratio of dichloromethane and chloroform.

2.3.2. Preparation of Mn(III) porphyrins, [Mn^{III}(TMPP)X]. All Mn(III) porphyrin syntheses were based on an adaptation of combined literature methods [25, 26]. The bis(acetylacetonato) Mn(III) complexes with axial halo- or pseudo-halo groups, i.e. Cl⁻, Br⁻, N₃⁻ or NCS⁻, serve as useful intermediates for Mn(III) porphyrins [27].

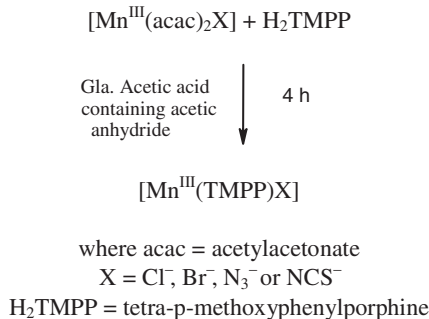
For preparation of chloro-complex, 0.979 g (0.003 mol) of [Mn^{III}(acac)₂Cl] and 2.5 g (0.003 mol) of H₂TMPP were dissolved in 150 mL of glacial acetic acid containing 45 mL of acetic anhydride and refluxed for 4 h on a hot plate. After refluxing, volatile materials were removed on a steam-bath and resulting bright green complex was dried

under vacuum over P_2O_5 . Recrystallization was done with 1 : 1 ratio of chloroform and methanol, and then air dried. The yield was 3.19 g (91%). The Br^- , N_3^- and NCS^- complexes were prepared analogously. All these complexes are non-hygroscopic. This method gives higher yield and takes less time in comparison to previous reported literature methods for the synthesis of other Mn(III) porphyrins.

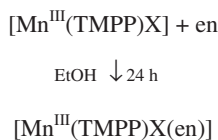
2.3.3. Preparation of ethylenediamine complexes, $[Mn^{III}(TMPP)X(en)]$. For preparation of the chloro complex, 0.822 g (0.001 mol) of $[Mn^{III}(TMPP)Cl]$ was dissolved in 4.0 mL of ethanol and then added to it 2.0 mL (0.030 mol) ethylenediamine. The whole content was stirred for 25 min at room temperature then refluxed for 24 h. The reaction mixture was cooled at room temperature for 1 h and dried under vacuum over P_2O_5 . Recrystallization was done with ethanol. Yield was 0.668 g (75%). The Br^- , N_3^- and NCS^- complexes were prepared analogously. All these complexes are hygroscopic and stored in a desiccator.

3. Results and discussion

The Mn(III) complexes with porphyrin were synthesized by the following reaction scheme:



These $[Mn^{III}(TMPP)X]$ complexes were dissolved in ethanol and refluxed with ethylenediamine to give final product. The proposed reaction scheme may be given as:



These complexes were soluble in ethanol, methanol, pyridine, chloroform, DMSO and partially in water. The molar conductance values in EtOH with $10^{-3} \text{ mol L}^{-1}$ concentration are in the range $12\text{--}26 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, indicating non-electrolytes [28]. The physical properties of these complexes have been given in table 1.

Table 1. Physical properties of Mn(III) porphyrins.

Ligand/complexes	Molar condu.	Color	Yield (%)	C	H	N	O	S	Br	Cl	Mn	Formula weight
H ₂ TMPP	—	Purple	23	78.44 (78.38)	5.21 (5.18)	7.62 (7.55)	8.71 (8.69)	—	—	—	—	734.37
[Mn(TMPP)Br]	28	Green	93.22	66.4 (66.2)	4.18 (4.12)	6.46 (6.41)	7.37 (7.32)	—	9.21 (9.18)	—	6.33 (6.30)	867.20
[Mn(TMPP)NCS]	19	Green	92.38	69.56 (69.52)	4.20 (4.18)	8.28 (8.23)	7.57 (7.51)	3.97 (3.89)	—	—	6.49 (6.41)	845.37
[Mn(TMPP)N ₃]	20	Green	95.74	69.46 (69.40)	4.32 (4.28)	11.82 (11.79)	7.71 (7.69)	—	—	—	6.62 (6.59)	829.31
[M(TMPP)Cl]	22	Green	91.84	70.01 (69.85)	4.41 (4.38)	6.81 (6.75)	7.77 (7.78)	—	—	4.30 (4.28)	6.67 (6.62)	822.74
[Mn(TMPP)Br(en)]	18	Black	67.66	64.71 (64.65)	4.78 (4.75)	9.06 (8.98)	6.90 (6.85)	—	8.62 (8.59)	—	5.92 (5.88)	927.27
[Mn(TMPP)NSC(en)]	24	Black	68.65	67.59 (67.55)	4.89 (4.85)	10.82 (10.79)	7.06 (7.00)	3.54 (3.51)	—	—	6.06 (6.01)	905.44
[Mn(TMPP)N ₃ (en)]	12	Black	70.89	67.46 (67.39)	4.98 (4.92)	14.17 (14.12)	7.19 (7.15)	—	—	—	6.17 (6.15)	889.39
[Mn(TMPP)Cl(en)]	12	Black	75.56	67.96 (67.91)	5.03 (4.98)	9.51 (9.48)	7.24 (7.19)	—	—	4.01 (3.96)	6.22 (6.18)	882.82

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

Mn(TMPP)Cl	Mn(TMPP)Br	Mn(TMPP)N ₃	Mn(TMPP)NCS	Assignment
428	425	425	426	$\nu(\text{Mn-N})$
1623	1623	1620	1623	$\nu(\text{C=C})_{\text{py}}$
1330	1325	1325	1323	$\nu(\text{C=N})_{\text{py}}$
1517	1517	1512	1515	$\nu(\text{C=C})_{\text{ph}}$
3025	3023	3025	3026	$\nu(\text{C-H})_{\text{ph}}$
1174	1173	1173	1173	$\nu(\text{OCH}_3)$
–	–	–	2074	$\nu(\text{NCS})$
–	–	2023	–	$\nu(\text{N}_3)$

3.1. Infrared spectra

Infrared spectra of these complexes show sharp bands at $\sim 1622 \text{ cm}^{-1}$ suggesting $\nu(\text{C=C})_{\text{pyrrole}}$. A medium band at $\sim 1324 \text{ cm}^{-1}$ for $\nu(\text{C=N})_{\text{pyrrole}}$ appears at 1350 cm^{-1} in the free ligand. This band shows a downward shift of $\sim 25 \text{ cm}^{-1}$ indicating coordination of porphine nitrogen. A medium band at $\sim 1512 \text{ cm}^{-1}$ indicates $\nu(\text{C=C})_{\text{phenyl}}$. Another weak absorption at $\sim 1173 \text{ cm}^{-1}$ indicates $\nu(\text{OCH}_3)$ of phenyl. A strong band at $\sim 840 \text{ cm}^{-1}$ is assigned to *p*-disubstituted benzene. A sharp band at $\sim 956 \text{ cm}^{-1}$ indicates the presence of (C–H) rocking mode of pyrrole. All these peaks are in agreement with previous literature values [29, 30]. The spectra show two bands characteristics of coordinated NCS^- i.e. $\nu(\text{C-N})$ at $\sim 2074 \text{ cm}^{-1}$ and $\nu(\text{C-S})$ at 820 cm^{-1} suggesting coordination of NCS^- [31] in the thiocyanate complex. Two characteristic peaks of coordinated azide $\nu_{\text{as}}(\text{N-N})$ show the strong absorption at 1248 cm^{-1} and another broad peak at $\sim 2030 \text{ cm}^{-1}$, indicating coordination of N_3^- [32]. The $\nu(\text{Mn-N})$ was characterized by the presence of an absorption at $\sim 425 \text{ cm}^{-1}$ for all the complexes [30, 33] (table 2).

The asymmetric NH_2 stretching frequency for ethylenediamine is $3440\text{--}3250 \text{ cm}^{-1}$; in Zn(en)Cl_2 it is given at $3290\text{--}3230 \text{ cm}^{-1}$ showing the chelating en [34]. While in the case of these Mn(III) porphyrins $\nu(\text{NH}_2)$ appears at $\sim 3422 \text{ cm}^{-1}$ showing the presence of free amine group and at $\sim 3315 \text{ cm}^{-1}$ corresponding to the amine group that has coordinated with the metal ion. Characteristic bands of diamines appear between $1400 \text{ cm}^{-1}\text{--}700 \text{ cm}^{-1}$. A strong band at $\sim 1330 \text{ cm}^{-1}$ has been assigned to $\omega(\text{NH}_2)$. The CN stretching modes of all uncomplexed diamines appear at $1090\text{--}1070 \text{ cm}^{-1}$ [35]. In these newly synthesized complexes, $\nu(\text{CN})$ band appears at $1055\text{--}1046 \text{ cm}^{-1}$, the downward shift showing the coordination of nitrogen to manganese. The NH_2 rocking mode is a strong band at $\sim 637 \text{ cm}^{-1}$. Two medium peaks at $\sim 848 \text{ cm}^{-1}$ and $\sim 881 \text{ cm}^{-1}$ indicate CH_2 rocking mode. The $\nu(\text{C-C})$ has been assigned as a strong band at $\sim 1005 \text{ cm}^{-1}$ [36]. The data indicate ethylenediamine is coordinated to Mn(III) as a unidentate ligand (table 3).

3.2. Electronic spectra

Depending on the type of donor acceptor bonds there are three classes of metalloporphyrins electronic spectra, normal, hypso and hyper, with the hyper spectra being further divided into p-type and d-type [37, 38]. The third type of spectra i.e.

Table 3. Selected vibrational frequencies (cm^{-1}) in IR spectra of Mn(III) porphyrins.

Mn(TMPP)Cl(en)	Mn(TMPP)Br(en)	Mn(TMPP)N ₃ (en)	Mn(TMPP)NCS(en)	Assignment
426	423	428	425	$\nu(\text{Mn-N})$
1621	1623	1623	1622	$\nu(\text{C=C})_{\text{py}}$
1323	1325	1330	1324	$\nu(\text{C=N})_{\text{py}}$
1517	1514	1515	1512	$\nu(\text{C=C})_{\text{ph}}$
3023	3021	3025	3023	$\nu(\text{C-H})_{\text{ph}}$
1175	1173	1174	1173	$\nu(\text{OCH}_3)$
–	–	–	2080	$\nu(\text{NCS})$
–	–	2030	–	$\nu(\text{N}_3)$
3315	3312	3310	3310	$\nu(\text{NH}_2)_{\text{coordinated}}$
3422	3421	3420	3422	$\nu(\text{NH}_2)_{\text{uncoordinated}}$

Table 4. Location and intensity of bands in absorption spectra of solutions of Mn(III) complexes with TMPP and ethylenediamine in methyl alcohol.

Complex	λ_{max} nm (log ϵ)			
	I (Q)	II	III	IV (B)
[Mn(TMPP)Br]	684 (5.82)	520 (5.71)	–	444 (5.64)
[Mn(TMPP)NCS]	681 (5.83)	560 (5.74)	–	451 (5.65)
[Mn(TMPP)N ₃]	677 (5.83)	556 (5.74)	515 (5.71)	448 (5.65)
[M(TMPP)Cl]	682 (5.83)	558 (5.74)	514 (5.71)	460 (5.66)
[Mn(TMPP)Br(en)] ^a	625 (5.79)	589 (5.77)	485 (5.68)	431 (5.63)
[Mn(TMPP)NSC(en)]	604 (5.78)	567 (5.75)	471 (5.67)	440 (5.64)
[Mn(TMPP)N ₃ (en)]	652 (5.81)	591 (5.77)	465 (5.66)	435 (5.63)
[Mn(TMPP)Cl(en)]	651 (5.81)	–	466 (5.66)	427 (5.63)

^aSolution of the complex in toluene.

d-hyper type are observed for metalloporphyrins having unoccupied orbitals in metals with symmetries $e_g(d(\pi)) - d_{yz}$ and d_{xz} . The intense band at 440–480 nm in spectra of the complexes [39] is assigned to charge transfer from the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals of porphyrin to the $e_g(d(\pi))$ orbitals of the metal, a charge-transfer band [40].

Electronic spectra of porphyrins exhibit an intense band at 400 nm that are assigned as Soret or B band. Several weaker absorptions also occur at higher wavelengths, 480–700 nm, that are known as Q bands. For [Mn^{III}(TPP)X] complexes [30] these bands are at ~615, ~580, ~525, ~481 and ~400, where X = Cl[–], Br[–], Ac[–] or NCS[–], while in manganese(III) 5,10,15,20-tetra(N-ethyl-3-carbazolyl) porphyrin, [Mn^{III}(TCEP)] [41], these bands appear at 433, 523, 562, and 654 nm.

For [Mn(TMPP)X], where X = Br[–], NCS[–], N₃[–] or Cl[–], characteristic B bands (Soret band) have λ_{max} at 444, 451, 448, and 460 nm while the Q bands appear at λ_{max} 684, 681, 677, and 682, respectively. The [Mn(TMPP)X] complexes with ethylenediamine exhibit B bands at 431, 440, 435, and 427 nm and Q bands at 625, 604, 652, and 651, respectively. The assignment of B band has been done on the basis of previous studies [42, 43]. These B and Q bands exhibit small red shifts in the spectra, due to the effect of axial ligand and solvent [44, 45] (table 4).

Thus all data for manganese complexes with H₂TMPP and ethylenediamine follow similar trends when compared with TPP and TCEP manganese(III) complexes.

Table 5. Ligand field parameters calculated for Mn(III) porphyrins.

Complexes	$10D_q$ (cm ⁻¹)	B (cm ⁻¹)	β
[Mn(TMPP)Br]	26,371	976	0.85
[Mn(TMPP)NCS]	25,614	948	0.83
[Mn(TMPP)N ₃]	25,933	960	0.84
[Mn(TMPP)Cl]	24,703	914	0.80
[Mn(TMPP)Br(en)]	25,000	925	0.81
[Mn(TMPP)NSC(en)]	28,153	1042	0.91
[Mn(TMPP)N ₃ (en)]	29,620	1097	0.96
[Mn(TMPP)Cl(en)]	28,801	1066	0.93

Since all Mn(III) porphyrins have a high-spin d^4 configuration, the strongly antibonding b_{1g} orbital remains empty. The energy of the a_{1g} level is somewhat depressed. Further the $e_g(d\pi)$ metal level is also depressed as it is bonding with respect to the back π bonding with the porphyrin. The relative position of the e_g and b_{2g} levels may be reversed. The lowest energy allowed charge transfer bands are the porphyrin to metal $a_{2u}, a_{1u} \rightarrow e_g(d\pi)$ transitions [46]. Bands I, II, and IV can be assigned to $a_{2u}, a_{1u} \rightarrow e_g(d\pi)$ charge transfer transitions. The assignment of band IV to charge transfer transition has been previously suggested [47]. Ligand field parameters such as $10D_q$, B and β have 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 the formula $D_q/B = 2.7$ using Tanabe-Sugano diagram while β values have been calculated using formula

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

The values of Racah interelectronic repulsion parameter (B) are below the free ion value for Mn(III) ion (1140 cm^{-1}) [48], which indicates covalent metal ligand bonds in all the complexes, with the covalency factor β varying in the range 0.88 ± 0.08 (table 5).

3.3. Magnetic susceptibility measurements

The magnetic momentum values of these complexes are in the range 4.65–4.87 B.M. [25, 49], indicating the presence of four unpaired electrons confirming high spin $3d^4$ configuration in all the complexes.

3.4. ESI-mass spectra

Electrospray-ionization mass spectroscopy was used for identity and purity analysis of the Mn(III) porphyrins [50–52]. The molecular weight of the complexes have also been calculated. The spectra give m/z 845 for $[\text{C}_{49}\text{H}_{36}\text{N}_5\text{O}_4\text{SMn}]^+$, m/z 787 for $[\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{Mn}]^+$ and m/z 734 for $[\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4 + 2\text{H}]^+$ for $[\text{Mn}(\text{TMPP})\text{NSC}(\text{en})]$. For $[\text{Mn}(\text{TMPP})\text{Cl}(\text{en})]$, m/z 847 for $[\text{C}_{50}\text{H}_{44}\text{N}_6\text{O}_4\text{Mn}-\text{Cl}]^+$, m/z 805 for $[\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{Mn} + \text{H}_2\text{O}]^+$ and m/z 773 for $[\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_4 + \text{K}]^+$ have been obtained. For $[\text{Mn}(\text{TMPP})\text{Br}(\text{en})]$, m/z at 868 for $[\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{BrMn} + \text{H}]^+$, m/z at 805 for $[\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{Mn} + \text{H}_2\text{O}]^+$ and m/z at 734 for $[\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4 + 2\text{H}]^+$ and for $[\text{Mn}$

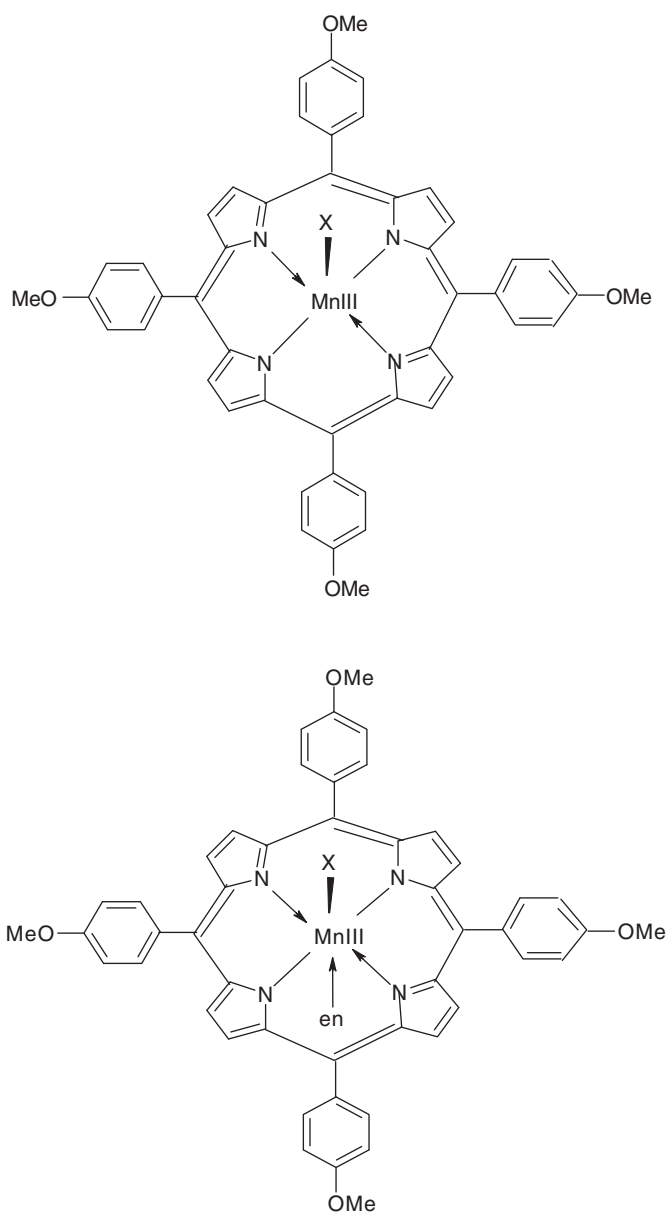


Figure 1. Proposed structure for Mn(III) porphyrins.

(TMPP) $N_3(en)$], m/z at 830 for $[C_{48}H_{36}N_7O_4Mn + H]^+$, m/z at 805 for $[C_{48}H_{36}N_4O_4Mn + H_2O]^+$ and m/z at 734 for $[C_{48}H_{36}N_4O_4 + 2H]^+$ have been found.

3.5. Structure

On the basis of elemental analysis, U.V., I.R., conductivity measurements, magnetic susceptibility measurements and ESI-mass spectra, the first four complexes have been

proposed to be square pyramidal while the proposed geometry for Mn(III) porphyrins with ethylenediamine is octahedral as reported earlier [18, 19]. These proposed structures are shown in figure 1.

4. Conclusion

Tetra-p-methoxyphenylporphinato Mn(III) complexes have been prepared. ESI-mass spectra indicate monomeric complexes. On the basis of the positions of NH₂ stretching frequency in I.R. spectra of tetra-p-methoxyphenylporphinato manganese(III) complexes with ethylenediamine, it has been concluded that ethylenediamine is unidentate. Generally, the metal porphyrins are insoluble in water but in the case of Mn(III) porphyrins with ethylenediamine a significant feature is that these are moderately soluble in water. Water solubility is required to use porphyrins for medicinal purposes [53]. Sun *et al.* [54] have synthesized porphyrin-nicacid dyad Mn(III) complexes to see the combined effect of porphyrin and nicacid on DNA cleavage. Here we report Mn(III) complexes with tetra-p-methoxyphenylporphine and ethylenediamine. It will be interesting to see in which way these new complexes will affect DNA cleavage, a property which has been seen in Mn(III) porphyrin complexes as tumor targeting agents in photodynamic therapy [55, 56].

Acknowledgements

The authors acknowledge UGC-DSA Fellowship (New Delhi) for financial support and would like to thank Prof. V.K. Yadav and Prof. Sundar S. Manoharan from IIT, Kanpur, for ESI-mass spectra and magnetic susceptibility measurements.

References

- [1] P. Souza, M.A. Mandiola, A. Arquero, V. Fernandez, E. Gulicrerr-Puebla, C. Ruiz Valero. *Naturforsch Z.*, **49b**, 263 (1994).
- [2] N.R. Champness, C.S. Frampton, G. Geid, D.A. Toucher. *J. Chem. Soc., Dalton Trans.*, 3031 (1994).
- [3] A.R. Adam, M. Antolovich, D.S. Baldwin, P.A. Duckworth, A.J. Leong, L.F. Lindoy, M. McPartlin, P.A. Tasker. *J. Chem. Soc., Dalton Trans.*, 1013 (1993).
- [4] J.P.L. Cox, K.J. Jankowaski, K. Ataky, D. Parker, M.A. Eaton, N.R. Beeley, A.J. Millican, A. Harrison, C. Walker. *J. Chem. Soc., Chem. Commun.*, 797 (1989).
- [5] L.F. Lauffer. *Chem. Rev.*, **87**, 901 (1987).
- [6] M. Ravikanth, T.K. Chandrashekhar. *Structure-Bonding*, **82**, 105 (1995).
- [7] O.A. Golubchikov, O.I. Koifman, G.V. Ponomarev. In *Porphyrins: Spectroscopy, Electrochemistry and Applications*, N.S. Enikolopyan (Ed.), p. 214, Nauka, Moscow (1987).
- [8] A.B. Solov'era, T.N. Rumyantseva. In *Advances in Porphyrin Chemistry*, O.A. Golubchikov (Ed.), Vol. 3, p. 245, NII Khimii SpbGU, St. Petersburg (2001).
- [9] A. Budimir, T. Smuc, T. Weitner, I. Batinic-Haberle, M. Birus. *J. Coord. Chem.*, **63**, 2750 (2010).
- [10] I. Batinic-Haberle, J.S. Reboucas, I. Spasojevic. *Antioxid. Redox Signaling*, **13**, 877 (2010).
- [11] S. Banafi, E. Cassani, E. Caruso, M. Cazzaro. *Bioorg. Med. Chem.*, **11**, 3595 (2003).
- [12] M.S.M. Quintino, K. Araki, H.E. Toma, L. Angnes. *Talanta*, **74**, 730 (2008).
- [13] J.H. Khorasani, M.K. Amini, H. Motaghi, S. Tangestaninejad, M. Moghadam. *Sens. Actuators B: Chem.*, **87**, 448 (2002).
- [14] M. Mascini, A. Macagnano, D. Monti, M.D. Carlo, R. Paolesse, B. Chen, P. Werner, A. D'Amico, C. Di Natale, D. Compagnone. *Biosens. Bioelectron.*, **20**, 1203 (2004).

- [15] N.A. Chaniotakis, A.M. Chasser, M.E. Meyerhoff, J.T. Grives. *Anal. Chem.*, **60**, 185 (1988).
- [16] A. Tulinsky, B.M.L. Chen. *J. Am. Chem. Soc.*, **99**, 3647 (1977).
- [17] V.W. Day, B.R. Stults, E.L. Tassett, R.S. Marianelli, L.J. Boucher. *Inorg. Nucl. Chem. Lett.*, **11**, 505 (1975).
- [18] J.F. Kirner, W.R. Scheidt. *Inorg. Chem.*, **14**, 2081 (1975).
- [19] V.W. Day, B.R. Stults, E.L. Tassett, R.S. Marianelli, L.J. Boucher. *Inorg. Nucl. Chem. Lett.*, **11**, 505 (1975).
- [20] R.J. Errington. *Advanced Practical Inorganic and Metalloorganic Chemistry*, 1st Edn, Chapman and Hall, London (1997).
- [21] W.L.F. Armarego, D.D. Perrin. *Purification of Laboratory Chemicals*, 4th Edn, Butterworth-Heinemann, Oxford (1997).
- [22] B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell. *Vogel's Text Book of Practical Organic Chemistry*, 4th Edn, ELBS, London (1984).
- [23] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denny. *Vogel's Text Book of Quantitative Chemical Analysis*, 5th Edn, ELBS, London (1996).
- [24] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Karsakoff. *J. Org. Chem.*, **32**, 476 (1967).
- [25] E.B. Fleischer, J.M. Palmer, T.S. Srivastava, A. Chatterjee. *J. Am. Chem. Soc.*, **93**, 3163 (1971).
- [26] B.R. Stults, V.W. Day, E.L. Tassett, R.S. Marianelli. *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).
- [27] B.R. Stults, V.W. Day, R.S. Marianelli. *Inorg. Chem.*, **14**, 722 (1975).
- [28] S.F.A. Kettle. *Coordination Compounds*, p. 168, Thomas Nelson and Sons, The Pitman Press, London (1975).
- [29] D.W. Thomas, A.E. Martell. *J. Am. Chem. Soc.*, **78**, 1338 (1956).
- [30] T.N. Lomova, B.D. Berezin. *Russ. J. Coord. Chem.*, **27**, 85 (2001).
- [31] R.J.H. Clark, C.S. Williams. *Spectrochim. Acta*, **22**, 1081 (1966).
- [32] J.R. Dyer. *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall of India Private Limited, New Delhi (1969).
- [33] G. Wilkinson, R.D. Gillard, J.A. McCleverty. *Comprehensive Co-ordination Chemistry*, Vol. 2, p. 816, Pergamon Press, Oxford (1987).
- [34] B.H. Stuart. *Infrared Spectroscopy: Fundamentals and Applications*, p. 104, John Wiley & Sons, Chichester, West Sussex, England (2004).
- [35] I. Gamo. *Bull. Chem. Soc. Jpn.*, **34**, 760 (1961).
- [36] A.D. Allen, C.V. Senoff. *Can. J. Chem.*, **45**, 888 (1965).
- [37] C. Cretu, C. Bucovician, I. Armeanu, A.M. Lacrama, E. Cosma-Fagadar. *Rev. Chim. Bucharest*, **59**, 979 (2008).
- [38] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Karsakoff. *J. Org. Chem.*, **32**, 477 (1967).
- [39] E. Fagadar-Cosma, M.C. Mirica, I. Balcu, C. Bucovician, C. Cretu, I. Armeanu, G. Fagadar-Cosma. *Molecules*, **14**, 1370 (2009).
- [40] Y. Lamamoto, M.D. Assis, K.J. Ciuffi, C.M.C. Prado, B.Z. Prellwitz, M. Moraes, O.R. Nascimento, H.C. Sacco. *J. Mol. Catal. A: Chem.*, **116**, 365 (1997).
- [41] C.P. Tidewall, L.D. Fondren, D.E. Nikles. *Molbank*, M656 (2010).
- [42] J.W. Buchler, W. Kokisch, P. Smith. *Struct. Bonding (Berlin)*, **34**, 79 (1978).
- [43] H. Skeno, H. Kobayashi. *J. Chem. Phys.*, **75**, 283 (1981).
- [44] L.J. Boucher. *J. Am. Chem. Soc.*, **90**, 6640 (1968).
- [45] L.J. Boucher. In *Coordination Chemistry*, S. Kirschner (Ed.), p. 126, Plenum Press, New York, NY (1969).
- [46] L.J. Boucher. *J. Am. Chem. Soc.*, **92**, 2727 (1970).
- [47] H.A.O. Hill, A.J. MacFarlane, R.J.P. Williams. *J. Chem. Soc.*, 1704 (1969).
- [48] J.E. Huheey, E.A. Keiter, R.L. Keiter. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th Edn, p. 445, Pearson Education, Singapore (2005).
- [49] D.V. Behere, S. Mitra. *Inorg. Chem.*, **19**, 992 (1980).
- [50] I. Batinic-Haberle, I. Spasojevic, R.D. Stevens, B. Bondurant, A. Okado-Matsumoto, I. Fridovich, Z. Vujaskovic, M.W. Dewhirst. *Dalton Trans.*, 617 (2006).
- [51] I. Batinic-Haberle, I. Spasojevic, R.D. Stevens, I. Fridovich, P. Hambright. *J. Chem. Soc., Dalton Trans.*, 2689 (2002).
- [52] I. Batinic-Haberle, I. Spasojevic, R.D. Stevens, A. Okado-Matsumoto, I. Fridovich, P. Hambright, P. Neta. *Dalton Trans.*, 1696 (2004).
- [53] T. Murashima, S. Tsujimoto, T. Yamada, T. Miyazawa, H. Uno, N. Ono, N. Sugimoto. *Tetrahedron Lett.*, **46**, 113 (2005).
- [54] E. Sun, X. Cheng, D. Wang, C. Zhuang, A. Xia, T. Shi. *J. Coord. Chem.*, **62**, 1584 (2009).
- [55] J. Stubbe, J.W. Kozarich. *Chem. Rev.*, **87**, 1107 (1987).
- [56] R. Song, Y.S. Kim, Y.S. Sohn. *J. Inorg. Biochem.*, **89**, 83 (2002).