

Preparation and Spectral Studies of cobalt (II), nickel (II), copper (II) and zinc (II) Complexes of New *meso*-substituted Unsymmetrical Porphyrins

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Received: 23rd Oct 2016, Revised and Accepted: 29th Oct 2016

ABSTRACT

New chelates of cobalt (II), nickel (II), copper (II), zinc (II) derived from unsymmetrical porphyrins (A₃B) have been synthesized. Their structures have been elucidated on the basis of UV-visible, IR, NMR and Mass spectra. The X-band ESR spectra of one of the Cu (II) complex is recorded and their salient features are reported. The exploration of biological properties of the compounds are in progress.

Keywords: Unsymmetrical metalloporphyrins, *meso*-functionalization, spectral study, ESR.

1. INTRODUCTION

Metal complexes of porphyrins have played a central role in the development of coordination chemistry. Electronic properties of porphyrins can be modulated at will by introducing suitable substituents at *meso* and β -positions, *meso*-tetraarylporphyrins are the most widely studied model compounds owing to their ease of synthesis and functionalization [1]. Most of the studies carried out on *meso*-tetraarylporphyrins involve introducing substituents either at β -positions or on *meso*-aryl groups. Porphyrins are an important class of biological pigments and they display remarkable properties that qualify them as advanced materials [2]. Therefore, it was thought worthwhile to synthesize some metalloporphyrins. In the present work, we report the synthesis and characterization of cobalt (II), nickel (II), copper (II), zinc (II) complexes (**1a-1d**, **2a-2d** and **3a-3d**) (**Scheme -II**) from unsymmetrical porphyrins (**1-3**) (**Scheme-1**) using different metal acetates in chloroform/methanol solvent.

Two common methods used for metalation of porphyrins are the acetate method and dimethyl formamide method [3] But is not a general method for all porphyrins as DMF is high boiling liquid.

A third method, for metalation of porphyrins employs metal acetylacetonate complexes as metal carrier [3] this method also used high boiling solvent.

In present work we used modified acetate method for preparing new metalloporphyrins in low boiling solvent mixture. All the reactions are carried in string or heating the porphyrin with metal acetate using chloroform/methanol solvent. The solvent mixture employed allow the dissolution of both reactants, CHCl₃ favouring the porphyrin and CH₃OH dissolves the metal acetate. Excess methanol leads to crystallization of product. The present method is less drastic as compare to reported methods.

2. EXPERIMENTAL

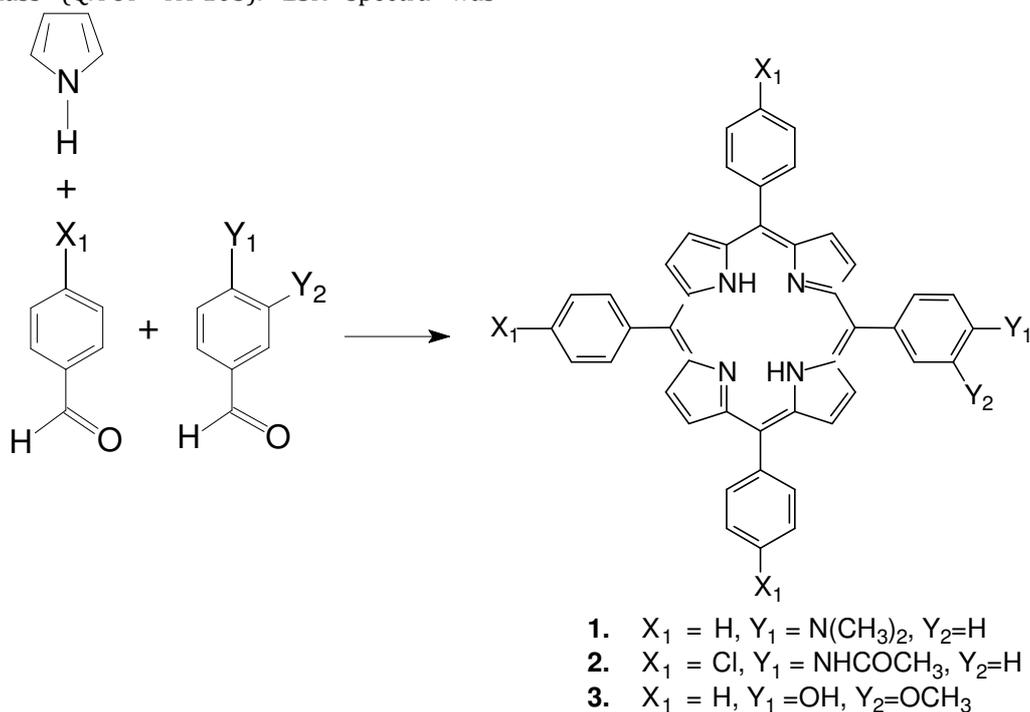
2.1. Materials

The three unsymmetrical porphyrins (1-3) were synthesized by modified Adler method [4] published elsewhere. All reagent grade chemicals were obtained from either Aldrich (USA) or S.D. Fine Chemicals (India). The pyrrole, benzaldehyde and propionic acid were freshly distilled before use. Other chemicals were used as received silica gel (60-120 mesh) was used for column chromatography.

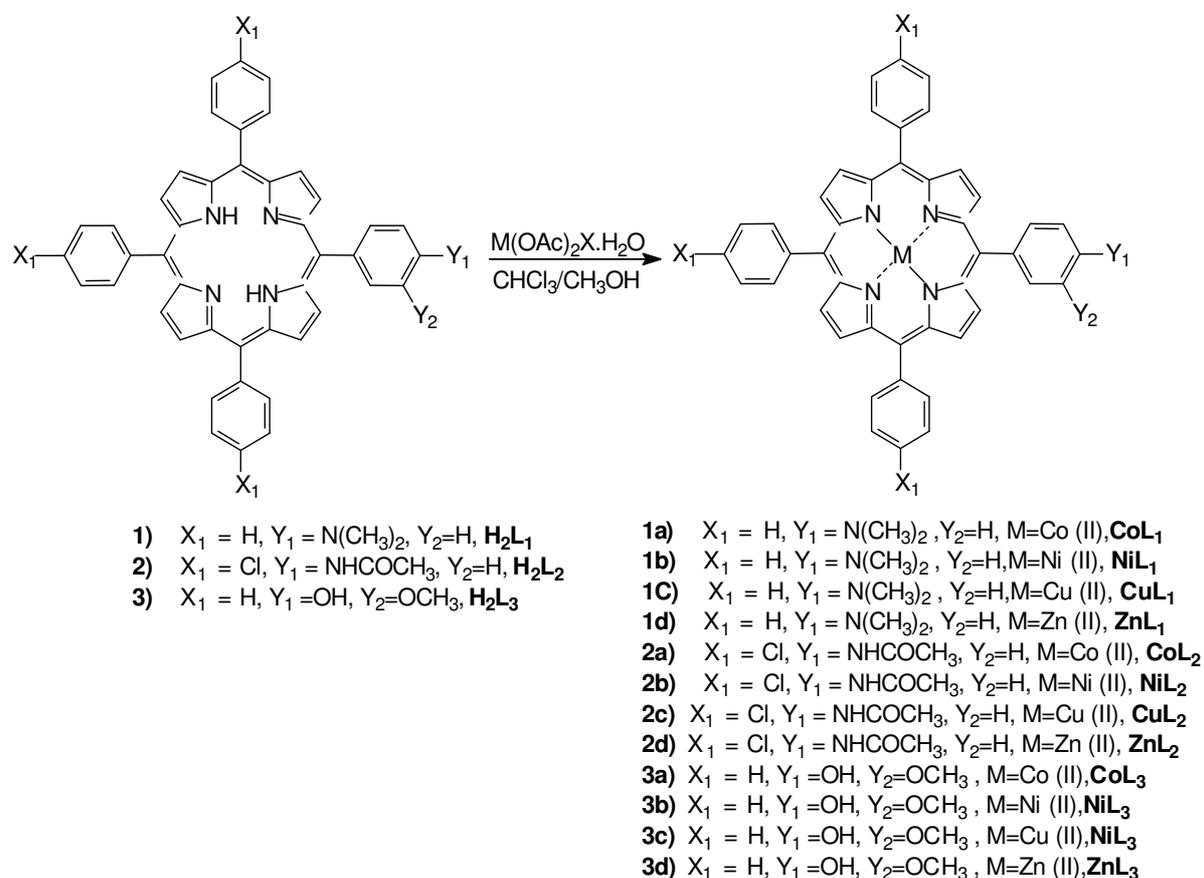
2.2. Physical measurements

C, H and N elemental analysis were determined on Perkin Elmer (240C) elemental analyzer. UV-visible absorption spectra were recorded on Shimadzu UV-spectrophotometer (UV-1601). The IR Spectra were recorded on Shimadzu Infrared Spectrophotometer (FT-IR-8400). Far IR was recorded on Magna IR Spectrometer (550 Nicolet). The ¹H-NMR spectra were performed on Varian (Mercury YH-300) of 300 MHz using tetramethylsilane as internal

standard. Mass spectra were recorded non micromass (Q.TOF YA-105). ESR spectra was recorded on Bruker EMX



Scheme - I : Synthesis of Porphyrins (1-3)



Scheme - II : Synthesis of metalloporphyrins (1a-1d, 2a-2d and 3a-3d).

EPR spectrometer (ER 041. XG-microwave bridge X-band) and EPR Spectrometer (Varian) with solid polycrystalline sample at room temperature and under liquid nitrogen (LNT).

2.3. Synthesis of macrocycles and their complexes

Synthesis of 5-[(4-N,N-dimethylamino)phenyl]-10,15,20-tris(phenyl)porphyrin (1). Synthesis of 5-[(4-acetamido)phenyl]-10,15,20-tris(4-chlorophenyl)porphyrin (2). Synthesis of 5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20-tris(phenyl)porphyrin (3).

2.3.1. Synthesis of [5-[(4-N,N-dimethylamino)phenyl]-10,15,20-tris(phenyl)porphyrinato] cobalt(II) complex (1a), CoL₁

A mixture of porphyrin (1) (72.9 mg, 0.1 mmol) in CHCl₃ (10 ml) and Co(OAc)₂·4H₂O (49.8 g, 0.2 mmol) in methanol (5 ml) was stirred at 60°C for 3 h. The completion of reaction was monitored by TLC. The reaction mixture was cooled to room temperature. The solvent was evaporated and the residue was extracted with chloroform. The organic layer was separated, washed with water, dried over anhydrous Na₂SO₄, and after evaporation of solvent furnished purple coloured solid as a title compound (1a); Yield (70.8 mg, 90 %).

UV-Visible (λ_{max}): 408, 502, 543 nm; IR (KBr): 526.5, 659.6, 750.3, 798.5, 947.0, 1004.8, 1184.2, 1309.6, 1352.0, 1444.6, 1521.7, 1602.7, 1890.1, 2798.5, 3053.1, 3361.7 cm⁻¹; Far IR: 169.0, 211.8, 239.0, 256.2, 264.7, 296.6, 315.3, 404.7 cm⁻¹; Mass (Q-TOF MSES 2.45e3) m/z: 714.3398 (M⁺);

Anal calcd for C₄₆H₃₃N₅·Co·4H₂O (%): C, 70.22; H, 5.25; N, 8.90

Found (%): C, 70.0; H, 4.91; N, 8.62

2.3.2. Synthesis of [5-[(4-N,N dimethylamino)phenyl]-10,15,20-tris(phenyl)porphyrinato] nickel (II) complex (1b), NiL₁

A mixture of porphyrin (1) (87.58 mg, 0.12 mmol) in CHCl₃ (10 ml) and Ni(OAc)₂·4H₂O (62.21 mg, 0.25 mmol) in methanol (5 ml) was stirred at 60°C for 4 h. After completion of reaction as indicated by TLC, the reaction mixture was cooled at room temperature. The solvent was evaporated and crude product was then purified by column chromatography (silica gel, CHCl₃/pet ether 6:4). The second redish pink band was collected and after evaporation of solvent furnished target material (1b); Yield (75.41 mg, 80 %).

UV-Visible (λ_{max}): 415, 529.0, 685.0 nm; IR (KBr): 704.0, 752.2, 798.5, 945.1, 1006.8,

1072.3, 1130.2, 1163.9, 1353.9, 1433.0, 1566.1, 1598.9, 2798.5, 3055.0, 3298.0 cm⁻¹; Far IR: 124.7, 144.9, 160.5, 180.7, 224.3, 280.3 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): 1.25 -1.55(br s, OH of H₂O), 7.25-8.00(m,15H, Ar-H), 8.8 (m,8H, pyrrole-H)

Anal calcd for C₄₆H₃₅N₅·Ni·4H₂O (%): C, 70.24; H, 5.25; N, 8.90

Found (%): C, 70.0; H, 4.92; N, 8.71

2.3.3. Synthesis of [5-[(4-N,N dimethylamino)phenyl]-10,15,20-tris(phenyl)porphyrinato] copper (II) complex (1c), CuL₁

A mixture of porphyrin (1) (72.98 mg, 0.1 mmol) in chloroform (10 ml) and Cu(OAc)₂·H₂O (32.92 mg, 0.2 mmol) in methanol (5 ml) was stirred at room temperature for 4 h. The reaction was monitored by TLC, then after removal of solvent, the residue was extracted with chloroform. The organic layer was dried over anhydrous Na₂SO₄ and after evaporation of solvent furnished red solid as a target material (1c); Yield (63.30 mg, 80 %).

UV-Visible (λ_{max}): 413.50, 541.50, 581.6, 617.50 nm; IR (KBr): 663.5, 705.9, 752.2, 800.4, 947.0, 1001.0, 1070.4, 1128.3, 1164.9, 1195.8, 1309.6, 1348.1, 1442.7, 1519.8, 1602.7, 1811.0, 2922.0, 3417.6 cm⁻¹;

Anal calcd for C₄₆H₃₃N₅·Cu·4H₂O (%): C, 69.81; H, 5.22; N, 8.84

Found (%): C, 69.42; H, 5.0; N, 8.40

2.3.4. Synthesis of [5-[(4-N,N-dimethylamino)phenyl]-10,15,20-tris(phenyl)porphyrinato] zinc (II) complex (1d), ZnL₁

A mixture of porphyrin (1) (87.58 mg, 0.12 mmol) in chloroform (10 ml) and Zn(OAc)₂·2H₂O (43 mg, 0.2 mmol) in methanol (5 ml) was then stirred at room temperature for 2 h. After completion of reaction as indicated by TLC, the solvent was then evaporated. The residue was washed with water and it was then extracted with CHCl₃. The organic layer was separated and dried over anhydrous Na₂SO₄ and after solvent evaporation under reduced pressure afforded purple solid as a target material (1d); Yield (63.45 mg, 80 %).

UV-Visible (λ_{max}): 427.50, 555.50, 598 nm; IR (KBr): 667.3, 704.0, 752.2, 798.5, 921.9, 947.0, 991.1, 1068.5, 1145.6, 1201.6, 1340.4, 1440.7, 1585.1, 1600.8, 2366.5, 2796.6, 3024.2, cm⁻¹;

calcd for C₄₆H₃₃N₅·Zn·4H₂O (%): C, 69.65; H, 5.21; N, 8.82

Found (%): C, 69.32; H, 5.0; N, 8.72

2.3.5 Synthesis of [5-[(4-(acetamido) phenyl)-10,15,20-tris(4-chlorophenyl) porphyrinato] cobalt (II) complex (2a), CoL₂

A mixture of porphyrin (2) (84.73 mg, 0.1 mmol) in CHCl₃ (10 ml) and Co(OAc)₂.4H₂O (49.8 mg, 0.2 mmol) in methanol (10 ml) was stirred at room temperature for 3 h. After completion of reaction as indicated by TLC, the solvent was removed under reduced pressure. The residue was chromatographed (Silica gel, CHCl₃/pet ether 5:5) and the second moving band was collected and removal of solvent under reduced pressure afforded pink solid as a title compound (2a); Yield (81.0 mg, 90 %).

UV-Visible(λ_{max}) : 412, 529.0 nm ; IR (KBr) : 717.5,802.3,1004.8,1089.7,1311.5, 1350. 1,1417.6, 1552.6, 2374.2, 2925.8, 3651.0 cm⁻¹;

Anal calcd for C₄₆H₂₈N₅OCl₃Co. 4H₂O (%): C, 61.10; H, 4.01; N, 7.74 s

Found (%) : C, 60.0; H, 3.90; N, 7.61

2.3.6. Synthesis of [5-[(4-(acetamido)phenyl)-10,15,20-tris(4-chlorophenyl) porphyrinato]]nickel (II) complex (2b), NiL₂

A mixture of porphyrin (2) (84.73 mg, 0.1 mmol) in CHCl₃ (10 ml) and Ni(OAc)₂.4H₂O (49.76 mg, 0.2 mmol) in methanol (10 ml) was stirred at 60 °C for 6 h. After completion of reaction as indicated by TLC, the solvent was then removed. The crude product was then purified by column chromatography (silica gel, chloroform/pet ether 8:2). The second moving band was collected and after evaporation of solvent afforded purple solid as a target material (2b); Yield (63.28 g, 70 %).

UV-Visible(λ_{max}):414.50, 517, 551 ,591, 647.50 nm; IR (KBr) : 680.8, 729.0, 798.5, 846.7, 966.3, 1018.3, 1091.6, 1180.4, 1220.9, 1313.4, 1348.1, 1421.4, 1560.3, 1670.2, 2395.4,2925.8 cm⁻¹;

Anal calcd for C₄₆H₂₈N₅OCl₃.Ni.4H₂O (%): C, 61.11; H, 4.01; N, 7.74

Found (%): C, 61.0; H, 3.82; N, 7.33

2.3.7. Synthesis of [5-[(4-(acetamido) phenyl)-10,15,20-tris(4-chlorophenyl)porphyrinato]] copper (II) complex (2c), CuL₂

A mixture of porphyrin (2) (84.73 mg, 0.1 mmol) in CHCl₃ (10 ml) and Cu(OAc)₂.H₂O (40 mg, 0.2 mmol) in methanol (5 ml) was stirred at room temperature for 4 h. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was washed with water and then extracted with chloroform. The organic layer was separated dried over anhydrous Na₂SO₄ and after removal of solvent furnished red solid as a target material (2c); Yield (81.79 mg, 90 %).

UV-Visible(λ_{max}): 415.5, 540.0, 616.50, 814.50 nm; IR (KBr) : 503.4, 626.8, 686.6, 802.3, 850.5, 1002.9, 1255.6, 1311.5, 1344.3, 1490.91, 1535.2, 1604.7, 2354.9, 3377.1cm⁻¹;

Anal calcd for C₄₆H₂₈N₅OCl₃Cu.4H₂O (%) : C, 60.79; H, 3.99; N, 7.70

Found (%) : C, 60.50; H, 3.54; N, 7.42

2.3.8. Synthesis of [5-[(4-(acetamido)phenyl)-10,15,20-tris(4-chlorophenyl)porphyrinato]] zinc (II)

complex (2d), ZnL₂ : A mixture of porphyrin (2) (84.73 mg, 0.1 mmol) in CHCl₃ (10 ml) and Zn(OAc)₂.2H₂O (43 mg, 0.2 mmol) in methanol (5 ml) was stirred at room temperature for 2 h. After completion of metallation reaction as indicated by TLC, the solvent was removed. The residue was washed with water and then it was extracted with chloroform. The organic layer was separated dried over anhydrous Na₂SO₄ and after evaporation of solvent furnished a purple solid as a title compound (2d) Yield (63.45 mg, 80 %).

UV-Visible(λ_{max}) : 416, 555.50, 596, 783.50 nm; IR (KBr) : 682.8, 719.4, 800.4, 999.1, 1089.7, 1176.5, 1205.4, 1247.9, 1336.6, 1398.3, 1485.1, 1523.7, 1595.0, 1668.3, 2923.9 cm⁻¹;

Anal calcd for C₄₆H₂₈N₅OCl₃Zn.4H₂O (%): C, 69.65; H, 5.21; N, 8.82

Found (%) : C, 69.32; H, 5.0; N, 8.72

2.3.9 Synthesis of [5-[(4-hydroxy-3-methoxy) phenyl]-10,15,20 tris(phenyl)porphyrinato] cobalt(II) complex (3a), CoL₃

A mixture of porphyrin (3) (73.28 mg, 0.1 mmol) in chloroform (15 ml) and Co(OAc)₂.4H₂O (37.35 mg, 0.15 mmol) in methanol (5 ml) was stirred at 60°C for 15 min. The solvent was removed under reduced pressure and residue was purified by column chromatography using chloroform as an eluant. The second pink band was collected and after evaporation of solvent afforded pink solid as title compound; Yield: 63.6 mg, (80%)

UV-Visible (λ_{max}) : 411.50, 529.50 nm; IR (KBr) : 705.9, 752.2, 798.5, 935.4, 1006.8, 1170.7, 1269.1, 1350.1, 1450.4, 1504.4, 1554.5, 1596.9, 2850.6, 2925.8, 3055.0, 3431.1 cm⁻¹

Anal calcd for C₄₅H₃₀N₄O₂Co.4H₂O (%): C, 68.43; H, 4.85; N, 7.09

Found (%) : C, 68.40; H, 4.60; N, 7.0

2.3.10 Synthesis of [5-[(4-hydroxy-3-methoxy) phenyl]-10,15,20-tris (phenyl) -porphyrinato nickel (II) complex (3b), NiL₃

A mixture of porphyrin (3) (73.28 mg, 0.1mmol) in chloroform (10 ml) and

Ni(OAc)₂.4H₂O (62.21 mg, 0.25 mmol) in methanol (10 ml) was stirred at 60°C for 4 h. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. The solvent was then evaporated under vacuum to afford crude product which was then purified by column chromatography (silica gel, CHCl₃ / pet. ether 5:5). The second band was collected and after evaporation of solvent yielded a pink solid as a title compound (3b); Yield : 67.1 mg, (85%)

UV-Visible (λ_{max}) : 415.50, 528.50, 647 nm; IR (KBr) : 430.1, 750.3, 796.5, 1006.8, 1074.3, 1203.5, 1259.4, 1352.0, 1510.2, 1558.4, 1654.8, 2922.9, 3172.7, 3591.2 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : 1.25-1.54 (br s, OH of H₂O), 3.95(s, 3H, OCH₃), 5.9(s, 1H, Ar-OH), 7.25-7.70(m, 15H, Ar-H), 8.0(m, 3H, Ar-H), 8.85(m, 8H, pyrrole-H)

Anal calcd for C₄₅H₃₀N₄O₂Ni.4H₂O (%) : C, 68.45; H, 4.85; N, 7.09

Found (%) : C, 68.25; H, 4.63; N, 7.00

2.3.11. Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20 tris(phenyl) porphyrinato] copper(II) complex (3c), CuL₃

A mixture of porphyrin (3) (87.93 mg, 0.12 mmol) in chloroform (10 ml) and Cu(OAc)₂.H₂O (39.92 mg, 0.2 mmol) in methanol (5 ml) was stirred at room temperature for 4 h. After completion of metallation as indicated by TLC, the reaction mixture was washed with water and extracted with chloroform. The organic phase dried over anhydrous Na₂SO₄ and after removal of solvent under reduced pressure furnished reddish pink solid as a title compound (3c); Yield : 85.77 mg, (90 %)

UV-Visible (λ_{max}) : 412.0, 539.50, 617 nm; IR (KBr) : 750.3, 798.5, 931.6, 1002.9, 1118.6, 1163.9, 1261.4, 1344.3, 1442.7, 1510.2, 1602.7, 2380.0, 3487.1, 3649.1, 3751.3 cm⁻¹; Far IR (cm⁻¹) : 144.411, 217.3, 232.9, 269.205, 331.7, 371.4, 405, 415, 439, 445.0, 521, 539 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : 0.97-1.54(br s-OH of H₂O), 3.85(s, 3H-OCH₃), 5.85(s, 1H, -OH), 7.20-7.9(m, 15H, Ar-H), 8.2(m, 3H, Ar-H), 8.90(m, 8H, Pyrrole-H)

Anal calcd for C₄₅H₃₀N₄O₂Cu. 4H₂O (%) : C, 68.04; H, 4.82; N, 7.05

Found (%) : C, 68.0; H, 4.42; N, 6.90

2.3.12. Synthesis of [5-[(4-hydroxy-3-methoxy)phenyl]-10,15,20 tris(phenyl)porphyrinato] zinc(II) complex (3d), ZnL₃

A mixture of porphyrin (3) (87.94 mg, 0.12 mmol) in chloroform (10 ml) and Zn(OAc)₂.2H₂O (43.8 mg, 0.2 mmol) in methanol (10 ml) was stirred at room temperature for 4 h.

After completion of reaction as indicated by TLC, the solvent was evaporated. The solid was extracted with chloroform and washed with water to remove excess metal acetate. Organic layer was dried over anhydrous Na₂SO₄, and removal of solvent under reduced pressure furnished a purple solid as a title compound (3d); Yield : 76.42 mg, (80%)

UV-Visible (λ_{max}) : 416, 517, 553, 594, 647.50 nm; IR (KBr) : 704.0, 798.5, 1001.0, 1263.3, 1340.4, 1512.1, 1556.4, 1596.9, 1652.9, 1780.2, 2376.1, 3651.0, 3685.7, 3751.3 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : 1.20-1.6(br s, -OH of H₂O), 3.9(s, 3H, OCH₃), 6.0(s, 1H, OH), 7.25-7.75(m, 12H, Ar-H), 8.2(m, 3H, Ar-H), 8.9(m, 8H, pyrrole -H)

Anal calcd for C₄₅H₃₀N₄O₂Zn.4H₂O (%) : C, 67.88; H, 4.81; N, 7.03

Found (%) : C, 67.70; H, 4.71; N, 7.0

3. RESULTS AND DISCUSSION

3.1 Electronic Absorption Spectra

Metalloporphyrins can be divided into two groups based on their UV-Vis and fluorescence properties. Regular metalloporphyrin contains closed -Shell metal ions (d⁰ or d¹⁰) for example Zn (II), in which the d π (dxz, dyz) metal based orbitals are relatively low in energy. These shows little effect on the porphyrin π to π^* energy gap in porphyrin electronic spectra. Hypso porphyrin are the metalloporphyrin in which the metal are of d^m, m = 6-9 having filled d π orbitals. In these porphyrins there is significant metal d π to porphyrin π orbital interaction, which shows metal to ligand π -backbonding. This results in an increased porphyrin π to π^* energy separation causing hypsochromic shift in electronic absorption.

The comparative UV-visible spectral data of free base porphyrins (1-3) and metalloporphyrins (1a-1d, 2a-2d and 3a-3d) are listed in table 1.

The absorption spectra of compound (1a-1d, 2a-2d and 3a-3d), indicate that upon metallation the porphyrin ring deprotonates, forming dianionic ligand. The two hydrogens on the nitrogen items in free base porphyrin reduce the ring symmetry from square (for metalloporphyrins) to rectangular that is from D_{4h} to D_{2h}. In general more symmetrical molecule gives simpler spectrum. The metal behaves as Lewis acids, accepting lone pairs of electrons from diaionic porphyrin ligand. From spectra of all ligands and complexes the band around 400 nm which is a Soret band with high extinction coefficient and generally four lower extinction band are Q-bands.

Table - 1: UV visible spectroscopic data of free base porphyrins (1-3) and metalloporphyrins (1a-1d, 2a-2d and 3a-3d) in chloroform.

| Porphyrins/ metalloporphyrins | Compound No. | UV-visible Parameters (λ_{\max}/nm) | |
|----------------------------------|--------------|--|--------------------------------|
| | | Soret | Q-bands |
| H ₂ L ₁ | 1 | 415 | 519.50, 558, 592.50, 651.50 |
| CoL ₁ | 1a | 408 | 501, 543 |
| NiL ₁ | 1b | 415 | 529, 685 |
| CuL ₁ | 1c | 413 | 541.50, 581.0, 617.50 |
| ZnL ₁ | 1d | 427.50 | 550.50, 598.0 |
| H ₂ L ₂ | 2 | 416.0 | 516.0 |
| CoL ₂ | 2a | 412.0 | 529.0 |
| NiL ₂ | 2b | 414.50 | 517, 551, 591, 647.50 |
| CuL ₂ | 2c | 415.0 | 540, 616.50, 814.50 |
| ZnL ₂ | 2d | 416.0 | 555.50, 596, 783.50 |
| H ₂ L ₃ | 3 | 413 | 516.50, 552, 591, 648 |
| CoL ₃ | 3a | 411.50 | 529.50 |
| NiL ₃ | 3b | 415.50 | 528.50, 647 |
| CuL ₃ | 3c | 412 | 539.50, 617 |
| ZnL ₃ | 3d | 416 | 517, 553, 594 |

All synthesized complexes are highly coloured. Unlike most transition metal complexes, the colour is due to absorption (s) within the porphyrin ligand involving the excitation of electrons from π to π^* porphyrin ring orbital [5]. When metal binds to porphyrin absorption spectrum changes owing to symmetry effects, but the π to π^* energy gap little affected and regular metalloporphyrin spectrum results. The Hypsochromic shift and loss of fluorescence are distinct characteristics of hypso porphyrins [5]. The absorption indicates that change in spectrum (fewer peaks) on metallation is due to increased symmetry relation to free base porphyrin. It has been established that the central metal ion [6] and substituent at meso positions [7-10] affect the optical spectra of porphyrin which will decrease in the energy transition (red shift and change in oscillator strength of the absorption band).

When zinc binds to free base porphyrin, absorption spectrum changes owing to symmetry effect but π to π^* energy gap is little affected and a regular metalloporphyrin spectrum result. In contrast, to the other metals (for example Ni, Co and Cu) peaks are shifted to shorter wavelength due to metal $d\pi$ (dxz and dyz) to porphyrin π^* bonding. In all complexes ϵ values of the metal derivatives are about 25-50% as compared to corresponding free base porphyrin.

3.2. IR spectra

The IR spectral data of porphyrins and corresponding metalloporphyrins ascertain some functional groups to exist. The $\nu_{\text{N-H}}$ absorption band of free base porphyrin is at about 3320 cm^{-1} , $\delta_{\text{N-H}}$ (in planarity) and $\delta_{\text{N-H}}$ (out of planarity) absorption bands are about 927 cm^{-1} and 728 cm^{-1} . $\nu_{\text{C-H}}$ Absorption band of porphyrin is about 2920 cm^{-1} . Some peaks appearing in the range of 980 to 710 cm^{-1} are related to skeletal ring vibrations of free base porphyrin. These bands disappeared in all metalloporphyrins after metal insertion reaction, and new strong band appears near 1000 cm^{-1} corresponding to skeletal ring vibration of metal porphyrin recoil the result of literature [11-13]. The Far IR spectra of metalloporphyrins show $\nu_{\text{M-N}}$ stretching vibration which were support the complexation.

3.3. ¹H-NMR

The ¹H-NMR data of free base porphyrins (1-3) and metalloporphyrins show that the peak at around -2.9 ppm is the more shielded N-H proton at the center of porphyrins ligand. This peak disappears after complexation of porphyrin with metal because two H atoms are replaced by metal ion [12]. There is great movement to high field on the basis of strong shield effect of porphyrin ring.

3.4. Mass spectra

Mass spectra of metalloporphyrins shows molecular ion peak which confirms formation of title compound.

3.5. Electron spin resonance study

A large number of investigations working on porphyrins and related systems have utilized this method in probing into the structural and dynamic aspects of porphyrins as well as their role in biological systems [3]. In case of paramagnetic porphyrin system one or more unpaired electrons may reside either on π ligand system or in central metal atom or in both.

In order to obtain information of geometry, the X-band EPR spectra of complex (3c) have been recorded in the powder state at LNT. The value of g-Tensors are depicted in Table 2 for compound 3c the anisotropy in g values as $g_{//} = 2.303$ and $g_{\perp} = 2.05$ and $A_{//} = 206.9$, the $g_{//}$ and g_{\perp} values for compound (3c) leads to D_{4h} symmetry of compound (square planar) around Cu (II) ion.

The splitting of spectra into four lines at LNT confirms the ground state of Cu (II) ion as $S=1/2$. The unpaired electron of the metal ion interacts with Cu (II) nucleus with the nuclear spin $I = 3/2$ resulting in the splitting of spectrum into four lines. This confirms that copper is in +2 oxidation state with $S=1/2$ as a spin state resulting in the single line main EPR spectra.

Moreover, the values of G calculated as $g_{//} - 2 / g_{\perp} - 2$ comes out to > 4 for compound (3c) which leads to the packing of molecular planes one above the other confirms the planar arrangement of porphyrin rings in three dimensional space.

Microwave Frequency : 9.762770 GHz

Microwave Power : 4 mW

Modulation Frequency : 100 kHz

Receiver Gain : 5.02×10^4

Table - 2: ESR spectral data for compound (3c) at LNT

| Compound No. | g_1 | g_2 | g_3 | g_4 | g_5 |
|--------------|-------|-------|-------|-------|-------|
| 3c | 2.37 | 2.25 | 2.05 | 1.96 | 1.82 |

3.6. Fluorescence study

Fluorescence spectrum of Zn metalloporphyrin (3d) was studied. The excitation spectra of fluorescence are in good agreement with absorption spectra. This implies that the fluorescence does not originate from some impurities. The excitation was carried out in visible range.

Table - 3 : Excitation and emission spectral data of compound (3d)

| Emission spectra in $CHCl_3$ | |
|------------------------------|---------------------------|
| $\lambda_{ex} = 553.0$ nm | $\lambda_{ex} = 603.0$ nm |
| $\lambda_{em} = 604.0$ nm | $\lambda_{em} = 604.0$ nm |

4. CONCLUSION

A new efficient approach to the synthesis of unsymmetrical porphyrins has been developed. The novel metalloporphyrins (1a-1d, 2a-2d, 3a-3d) were synthesized and characterized using UV,IR, 1H NMR, MASS and ESR spectroscopic methods.

Acknowledgement

P B. Gujarathi thanks University Grants Commission, New Delhi for teacher fellowship under faculty improvement programme. The author is also thankful to IIT Bombay and Pune University, Pune for providing spectral and data of the compounds.

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