RESEARCH PAPER

Chemistry



Synthesis, Characterization and Biological Studies of PorphyrinylChromium(III) benzimidazole Complexes

KEYWORDS	Octahedral,chromium(III) porphyrin,imidazoles antifungal behaviour					
* Ga	auri D. Bajju	Ved Kumar				
Associate Professor, Department of Chemistry University of Jammu-180006, Jammu and Kashmir, India * Corresponding author		Research Scholar, Department of Chemistry University of Jammu-180006, Jammu and Kashmir, India				
	Ashu	Deepmala				
Research Scholar, Department of Chemistry University of Jammu-180006, Jammu and Kashmir, India		Research Scholar, Department of Chemistry University of Jammu-180006, Jammu and Kashmir, India				

ABSTRACT Six co-ordinate chromium(III) complexes [CrCl(RTPP)L] (where R = H, CH3 and OCH3 group and L = 2-alkyl substituted benzimidazoles) were prepared by reacting the ligands with CrCl(RTPP). The complexes so obtained were characterized by elemental analysis, IR, U.V-visible and 1H and 13C NMR. All complexes show Cr-N stretching vibrations between 430-495 cm-1 and bands appearing in the range of 370-430 cm-1 shows the stretching vibration for v(Cr-Cl). The presence of axially ligated chromium(III) derivatives shows slight shift in the stretching of Cr-N in the range of 530-550 cm-1. The presence of two bands occurring between 400-610 nm confirms the, presence of Chronium(III) porphyrins with 3d3 electronic configuration of complexes. Spectral and magnetic studies suggest an octahedral geometry to these complexes. Biochemically complexes show negligible antibacterial and anti-oxidant behavior but well positive antifungal activity.

Introduction

Porphyrins and metalloporphyrins have been an active field of research work because of their active involvement in many reactions of chemical and biological interest^{1,2}. They have been widely studied as sensitizers and finding biomedical application in the treatment of malignant tumors, plaque destruction, psoriatic lesions and in treatment of viruses³⁻⁷. Porphyrins are important class of macrocyclic ligands in co-ordination chemistry of transition metals and often find applications in the fields of radio pharmaceuticals for cancertargeting⁸ agrochemicals, model system for biological macromolecules, dioxygen carrier etc. Also benzimidazoles belonging to fused heterocyclic system are associated with pharmaceutical activities such as antibacterial, insecticidal, fungicidal, antimicrobial and anti-inflammatory action⁹. Also metal based antioxidants have received recent attention for the capacity to protect organisms and cells from damage induced by oxidative stress¹⁰⁻¹². An effective antioxidant however should be able to terminate the attack of reactive species like free radicals and prevent them from attacking body cells. The antioxidant activity of synthetic compound can be measured by using scavenging ability of that compound to trap free radicals¹³.

These research results creates interest for chemists to search for the synthesis of metal complexes which may be bioactive in nature. The literature survey reveals that a large no. of porphyrin transition metal imidazole complexes have been prepared and characterised but no work has been done on chromium(III) substituted benzimidazole complexes. In view of the potential biological activity and practical applications of porphyrins complexes we have reported the synthesis, characterization and biological studies of few chlorochromium(III) porphyrin complexes with 2-alkyl substituted benzimidazoles as axial ligands.

Experimental

2.1 Materials and Instruments.

All the chemicals were of analytical grade. Pyrrole was distilled over KOH pellets under vacuum before use. All the organic solvents that were used for synthesis and chromatographic purpose were dried and repeatdly distilled prior to use. Elemental analysis C, H and N were obtained on vario El III and CHNS-93 2 Leco-Elemental analyser. UVvisible spectra were recorded on T90 + uv/vis spectrophotometer in rang of 350-700 nm. IR spectra were recorded on a Perkin Elmer spectrum 400 FTIR spectrophotometer using KBr pellets in the range of 4000-400 cm⁻¹. The ¹H NMR spectra were recorded on a BrukerAvance II 500(500 MHz) using TMS as standard and DMSO as solvent.

2.2 Biological Studies

2.2.1 Antibacterial studies

Qualitative analysis for screening of antibacterial activity was carried out by agarwell diffusion method¹³ with modification. The samples were tested for antibacterial activity against six bacterial strains. Stephylococcusaureus (S.A), *Micrococcus luteus* (M.L), Streptococcus pyogene (S.P), *Bacillus cereus* (B.C), *Pseudomonas aeruginosa* (P.A) and *Bacilliussubtilis* (B.S) by using chloremphincol as a positive reference to determine the sensitivity of bacteria.

2.2.2 Antifungal studies

Qualitative analysis for screening of antifungal activity of complexes were carried out against the pathogens *Saccharomyces cerevisiae* (S.C) and *Candida albicans* (C.A) by poisoned food method using Potato Dextrose Agar (PDA) nutrient as medium. The linear growth of fungus in control and treatment were recorded at different concentration of the compounds prepared.

2.2.3 Antioxidant studies

DPPH (1,1-diphenyl-2-picraylhydrzyl) radical scavenging activity was determined by measuring the bleaching of purple coloured methanol solution. The radical scavenging activity was determined according to method of Blots etal with modification¹⁴.

2.3. Synthesis of axially ligatedchlorochromium(III) porphyrin complexes.

2.3.1 Synthesis of macrocyclicporphyrins and Axial ligands

Macrocyclic RTPPH₂ and [CrCITPP] were prepared according to literature methods¹⁵⁻¹⁷. The 2-alkyl substituted benzimidazoles have been synthesized by procedure in literature⁹.

2.3.2 Synthesis of axially ligated CrCl(III) porphyrins. 2-Methyl CrCl(RTPP), 2-Ethyl CrCl(RTPP) and 2-propyl CrCl(RTPP).

Benzimidazoles and CrCl (RTPP) in 1:1 molar ratio were dissolved in 30 ml of dry $CHCl_3$ and reaction mixture was stirred on magnetic stirrer. The completion of reaction was indicated by TLC and was extracted with 95% water and 5% methanol. The extract containing compound was evaporated by vacuum pump and dried material was dissolved in $CHCl_3$ and filtered through anhydrous Na_2SO_4 and evaporated by vacuum pump. The final product was purified by column chromatography using basic alumina and $CHCl_3$ as eluent. The dried product was crystallized with $CHCl_3$ and recrystallised with pet-ether.Yield was 20-25%.

2.3.3.1 [(2-Mebmz)CrCl (TPP)]

UV-Vis (**CHCl**₃): λ_{max} (in nm)(log ε) 447.5(4.835) for B-band and 562.3(4.228) and 601.2(4.127) for Q-bands. IR(KBrcm⁻¹) 370-340(Cr-Cl) and 470-490 and 530-550 for (Cr-N); ¹H NMR(CDCl₃ + DMSO): δ9.0(s, 8H, β-pyrrole protons), 8.18(d, 10H, J=7.0, H₂), 7.99(m, 14H, H_{m,p}) for mesoaryl protons and 2,00 (s, 3H, CH₃), 6.11-6.14(m, 2H,ArH) and 7.00-7.23(m,2H, ArH) for bmz protons; ¹³C NMR(CDCl₃ + DMSO), 128.4, 128.8, 131.5, 135.0, 142.6, 145.0, 15.2, 24.6, 115.4, 121.6, 139.2 and 151.7 PPm.Anal. Calcd. For C₅₂H₃₆N₄CrCl(831.50): C, 75.04; H, 4.32; N, 10.10: Found: C, 75.0; H, 4.25; N, 10.0%.

2.3.3.2 [(2-Etbmz)CrCl(TPP)] Uv-vis(CHCl_3): λ_{max} (in nm)(logs) 446.8(4.854) for B-band and 562.1(4.253), 600.8(4.137) for Q-bands. I.R(KBrcm⁻¹): 370-430 for v(Cr-Cl), 470-490 and 530-550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO): δ 9.2(s, 8H, β -pyrrolo protons), 8.18(d, 10H, J = 7, H_o) and 7.94(m,14H, H_{m,p}) for mesoaryl protons and 2.02(d, 3H, CH₃), 3.01(q, 2H, CH₂), 6.13-6.16(m, 2H, ArH) and 7.21-7.23(m, 2H, ArH) for bmz protons. ¹³C NMR(CDCl₃ + DMSO):123.9, 28.5, 128.9, 131.5, 134.9, 142.6, 145.0, 14.8, 23.9, 114.6, 121.2, 138.9 and 151.1 PPm. Anal. Calcd. For C₅₃H₃₈N₆CrCl(845.50): C, 75.22; H, 4.49; N, 9.93: Found C, 75.10; H, 4.40; N, 9.89%.

2.3.3.3 [(2-propbmz)CrCl(TPP)]Uv-vis(CHCl₃): λ_{max} (in nm) (log_E), 448(4.872) for B-band and 563(4.2250); 601.5(4.146) for Q-bands. IR(KBrcm⁻¹) 370-430 for v(Cr-Cl); 470-490 and 530- 550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO): δ 9.3(s, 8H, β-pyrrole protons), 8.18(d, 10H, J = 7, H₀) 7.96(m, 14H, H_m) for mesoaryl protons and 2.02(d, 3H, CH₃), 3.01(m, 2H, CH₂), 4.01(d, 2H, CH₂), 6.14-6.16(m, 2H, ArH) and 7.21-7.23(m, 2H, ArH) for bmz protons. ¹³C NMR(CDCl₃ + DMSO):δ 124, 128.5, 131.6, 134.8, 142.4, 145.0, 14.8, 23.8, 114.5, 121.5 and 138.6 and 150.0 PPm. Anal Calcd. For C₅₄H₄₀N₆CrCl(859.50): C, 75.39; H, 4.65; N, 9.77. Found: C, 75.28; H, 4.50; N, 9.71%.

2.3.3.4 [(2-Mebz)CrCl(p-MeTPP)]:Uv-vis(CHCl₃), λ_{max} (in nm)(log ϵ) 447.4(4.827) for B-bnad and 563.3(4.237),

605.1(4.158) for Q-bands. IR(KBr cm⁻¹): 370-430 v(Cr-Cl).470-490 and 530-550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO):δ 9.1(s, 8H, β-pyrrole protons) 8.18(d, 10H, J = 7.0 H_o) and 7.93(m, 14H, H_{m,p}) for meso aryl protons and 2.02(s, 3H, CH₃), 6.12-6.14(m, 2H, ArH) and 7.11-7.21(m, 2H, ArH) for bmz protons. ¹³C NMR(CDCl₃ + DMSO): 123.1, 128.7, 128.8, 131.5, 135.5, 141.6, 145.2, 14.9, 24.3, 112.5, 122.6, 139.6 and 150.8 PPm. Anal. Calcd.for C₅₆H₄₄N₆CrCl (887.50): C, 75.18; H, 4.95; N, 9.46. Found: C, 74.98; H, 4.83; N, 9.08%.

2.3.3.5 [(2-Etbmz)CrCl(p-MeTPP)] Uvvis(CHCl₃): λ_{max} (in nm)(logs), 4476(4.867 for B band and 562.4(4.248) and 601.4(4.152) for Q-bands. IR(KBrcm⁻¹): 370-430 for v(Cr-Cl) and 470-490 and 530-550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO) δ 9.3(s, 8H, β -pyrrole protons), 8.18(d, 10H, J = 7, H₀) and 7.98(m, 14H, H_{m,p}) for meso-aryl protons and 2.03(d, 3H, CH₃); 3.01(q, 2H, CH₂), 6.13-6.14(2H, m, Ar-H) and 7.21-7.23(2H, m, ArH) for bmz protons. ¹³C NMR(CDCl₃ + DMSO): 123.6, 128.5, 128.9, 132.6, 135.5, 140.2, 15.3, 24.5, 114.5, 121.0, 139.0 and 151.4 PPm. Anal. Calcd. For C₅₇H₄₆N₆CrCl(901.50): C, 75.87; H, 5.10; N, 9.31. Found: C, 74.99; H, 4.93; N, 9.06%.

2.3.3.6 [(2-propbmz)CrCl(p-MeTPP)]:UV-vis(CHCl₃)λ_{max}(in nm)(logs), 446.3(4.825) for B-band and 561.4(4.243), 608.3(4.142) for Q-bands. IR(KBr cm⁻¹): 370-430 for v(Cr-Cl) and 470-490 and 530-550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO): δ 9.0(s, 8H, for β-pyrrole protons), 8.18(d, 10H, J = 7.0, H₂), 9.7(m, 14H, H_{m,2}) for meso aryl protons and 2.03(d, 3H, CH₃), 3.0(m, 2H. CH₂), 4.01(d, 2H, CH₂), 6.14-6.15(m, 2H, ArH) and 7.21-7.23(m, 2H, ArH) for bmz protons. ¹³C NMR(CDCl₃ + DMSO): 123.5, 128.3, 128.8, 131.4, 135.0, 142.2, 145.3, 15.3, 24.5, 114.6, 121.2, 139.1 and 151.5 PPm. Anal. Calcd. For C₅₈H₄₈CrCl(915.50): C, 76.02; H, 5.24; N, 9.17. Found: C, 75.98; H, 5.10; N, 9.03%.

2.3.3.7 [(2-Mebmz)CrCl(p-oMeTPP)]:uv-vis(CHCl₃) λ_{max} (in nm)(logs), 447.8(4.827) for B-band and 563.3(4.362), 601.4(4.143) for Q-bands. IR(KBr cm⁻¹): 370-430 for v(Cr-Cl) and 470-490 and 530-550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO): δ 9.3(s, 8H, β-pyrrole protons) and 2.02 (s, 3H, CH₃), 6.10-6.13(2H, m, ArH), and 7.02-7.24(2H, m, ArH) for bmzprotons 8.18(d, 10H, J=7, H₂) and 7.95(m, 14H, H) for mesoaryl protons. ¹³C NMR(CDCl₃ + DMSO) 121.2, 128.4, 128.8, 132.5, 135.0, 142.0, 145.0, 15.2, 24.6, 114.5, 121.3, 138.2 and 151.6 PPm. Anal. Calcd. For C₅₆H₄₄N₆Cr-Cl(951.50): C, 70.62; H, 4.62; N, 8.82. Found: C, 70.14; H, 4.50; N, 8.29%.

2.3.3.8 [(2-Etmz)CrCl(p-oMeTPP)]: Uv-vis (CHCl₃)λ_{max}(in nm)(log₆), 448.2(4.831) for B-band and 563.4(4.405), 601.4(4.120) for Q-bands. IR (KBr cm⁻¹): 370-430 for v(Cr-Cl) and 470-490 and 530-550 for v(Cr-N).¹H NMR(CDCl₃ + DMSO): δ9.3(s, 8H, β-pyrrole protons), 8.18(d, 10H, J=7.0, H₂) and 7.95(m, 14H, H_{m.p}) for meso aryl protons and 2.02(d, 3H, CH₃), 3.01(q, 2H, CH₂, 6.13-6.16(m, 2H, ArH) and 7.21-7.23(m, 2H, ArH) for bmz protons. ¹³C NMR(CDCl₃ + DMSO): 123.5, 128.3, 128.8 131.5, 135.0, 141.5, 145.0, 15.1, 24.6, 112.9, 121.3139.4 and 150 PPm. Anal. Calcd. For C₅₇H₄₆N₆O₄CrCl(965.50): C, 70.84; H, 4.76; N, 8.70. Found: C, 70.46; H, 4.58; N, 8.45%.

2.3.3.9 [(2-Propbmz)CrCl(p-oMeTPP)]:Uv-vis(CHCl₃)λ_{max}(in nm)(logs),, 445.6(4.835) for B-band and 562.0(4.356), 601.8(4.089) for Q-bands. I.R(KBr cm⁻¹): 370-430 for v(Cr-Cl) and 470-490 and 530-550 for v(Cr-N). ¹H NMR(CDCl₃ + DMSO): δ 9.3(s, 8H, β-pyrrole protons), 8.18(d, 10H, J=7.0, H_o), 7.96(m, 14H, H_{m,p}) for meso aryl protons and 2.02(d,

RESEARCH PAPER

3H, CH₃), 3.02(m, 2H, CH₂), 4.01(d, 2H, CH₂), 6.14-6.18(m, 2H, ArH) and 7.21-7.23(m, 2H, ArH) for bmz protons.¹³C NMR(CDCl₃ + DMSO): 124, 128.5, 131.6, 134.8, 142.5, 145.6,14.9, 23.6, 144.6, 121.6 and 138.6 PPm. Anal. Calcd. For $C_{58}H_{48}N_{6}O_{4}CrCl$ (979.50) C, 71.05; H, 4.90; N, 8.57. Found C, 71.01; H, 4.79; N, 8.09%.

3. Results and discussion

The general synthetic route to these peripherally tetrasubstituted phenyl porphyrin derivative (RTPP), their corresponding metallated and axially ligated chlorochromium(III) porphyrinsis shown in following scheme.



Volume : 5 | Issue : 1 | Jan 2015 | ISSN - 2249-555X

All these new chlorochromium(III) porphyrinswere characterized by spectroscopic data uv-visible, IR, ¹H and ¹³C NMR, mass spectra and elemental analysis. The characterization of new compound are consistent with the assigned formula. All these complexes are coloured and stable at room temperature soluble in CHCl₃, DMSO, CH₃OH, DMF and CH₃CN but insoluble in water and acetone.

3.1 Synthesis and Characterization

The structures of all substituted tetraphenylporphyrinchlor ochromium(III) benzimidazolesare characterized by various spectrochemical studies are given in experimental section.

3.1.1 Conductance and magnetic measurements.

The molar conductance values of complexes in DMSO at 10^{-3} M concentration were measured and shows in the low values of range $15-20\Omega^{-1}$ cm²mol⁻¹ revealing their neutral character. They exhibit magnetic moment in the range of 3.66-3.80 B.M at room temperature which are in agreement with three unpaired electrons and hence 3d³ configuration and monomeric octahedral nature of these complexes because magnetic moment values are close to spin only values of 3.88 B.M¹⁸.

3.1.2 Electronic spectra

The literature shows that in case of Cr(III)porphyrin complexes the intensesoret band absorption is seen at 458 nm and weaker Q-bands absorption at 572 and 612 nm. The weaker absorption at 400 nm is ofCr^{III}porphyrin complexes with anionic ligand which is attributed to $\pi(a_{2u}, a_{1u})$ to d(e₁) charge transfer from the porphyrin to metal centre¹⁹. The presence of these uv/vis absorption is a strong indication that neither molecular structure of macrocyclic nor oxidation state of chromium central metal is charged during ligation.

The observeduv-visible spectra of the complexes reported shows a slight blue shifts both for soret and Q-bands as the soretband generally appear near 445-448 nm and Q bands appear at ~560-563 and 600-603 nm respectively. The formation of new band around 610 nm indicates the axially ligated benzimidazole with chromium centre with octahedral geometry.

3.1.3 I.R Spectra

Since I.R spectral study is frequently used in elucidating the structures and determining the functional groups involved in co-ordination²⁰. The free base porphyrin shows v(N-H) stretching and bending vibrational modes between 3400-3320 cm⁻¹ and 960 cm⁻¹ respectively²¹. The incorporation of axially ligated chromium(III) ion in the centre of porphyrin causes shift in the values of vibrational frequencies as compared to corresponding free base porphyrins. The metallation of porphyrins is confirmed by the absence of vibrational frequency occurring due toimino group of porphyrin ring. Two additional bands for Cr-N and Cr-Cl are observed but with incorporation of 2-substituted imidazoles as sixth ligand on Cr(III), the vibrational frequency due to Cr-N is also observed in the range of 530-550 cm⁻¹. The presence of Cr-N bonds of porphyrin is shown by appearance of Cr-N stretching vibration at 470-490 cm⁻¹. Bands appearing in the range of 370-430 cm⁻¹ are attributed tov(Cr-Cl) vibrations²². There is no change due to stretching vibrational mode of N-H band of coordinatedimidazoles which shows that 2-substituted imidazoles are coordinated to Cr centre through N atom of ligand but not through imino group.

3.1.4 ¹H NMR spectra

In general the presence of axially ligated Cr(III) metal in the porphyrin ring results in broadening of lines and shift of resonance to down field accompanied by marginal changes in the pattern when compared with ¹H NMR spectra of free base porphyrin. All free base porphyrins reveal charactertics resonances of imino protons while metallated derivatives show the absence of imino proton signals. The signals of axially ligated-2-methyl, 2-ethyl and 2-propyl benzimidazoles fragment protons are shifted to higher fields in comparison to signals of porphyrins protons and also in comparison to protons signals of free 2-Me, 2-Ethyl and 2-propyl bmz respectively. These positions of protons signals shows that the axial ligand is under π -conjugated system of porphyrinmacrocycle. This is attributed due to dishielding effect resulting from the σ -donation of electron density upon bond formation as compared to shielding effect of porphyrin.

3.1.5 Mass spectral studies

Mass spectra is widely used in determination of molecular mass of porphyrins and metalloporphyrines. The mass spectra of these complexes are in good agreement with structure suggested by elemental analysis, spectral and magnetic studies. The mass of the molecular ion peak(m/z) for the compounds are.

[2-Me bmzCrCl(TPP)]+:830.935(Cal. C₅₂H₃₆N₆ClCr:831.50)

[2-EtbmzCrCl(TPP)]*: 845.301 (Cal. C₅₃H₃₈N₆ClCr: 845.50)

[2-Prop. bmzCrCl(TPP)]⁺: 858.690 (Cal. C₅₄H₄₀N₆ClCr: 859.50)

[2-MebmzCrCl(p-MeTPP)]*: 887.102 (Cal. C₅₆H₄₄N₆ClCr: 887.50)

[2-El bmzCrCl(p-MeTPP)]*: 900.895 (Cal. C₅₇H₄₆N₆ClCr: 901.50)

[2-Prop bmzCrCl(p-MeTPP)]*: 915.019 (Cal. C₅₈H₄₈N₆ClCr: 915.50)

[2-Me bmzCrCl(p-oMeTPP)]*: 950.896 (Cal. C₅₆H₄₄N₆O-₄ClCr:951.50)

[2-Et bmzCrCl(p-oMeTPP)]⁺: 965.066 (Cal. C₅₇H₄₆O₄ClCr: 965.50)

[2-Prop bmzCrCl(p-oMrTPP)]⁺: 978.638 (Cal. C₅₈H₄₈N₂O-₄ClCr:979.50)

3.1.6 Antibacterial studies

The synthesized chlorochromium(III) imidazole,complexes when tested for six bacterial strains as shown in table 1 shows negligible antibacterial activity.

3.1.7Antioxidant studies

When complexes samples were applied for stable DPPH free radical for detection of radical scavenging activity in chemical analysis shows no results of antioxidant behavior.

3.1.8 Antifungal Studies

The *in vitro* biological antifungal effect of the investigated samples when tested against the two pathogens *Saccharomyces cerevisiae* (S.C) and *Candida albicanes* (C.A) by the poisoned method using potato dextro Agar (PDA) nutrient as the medium is shown in the table 1. It is observed that for sample V-2, V-3, V-4, the sample V-2 has remarkable

inhibition of antifungal effect of 8 mm against prathogen C.A (*Candida albicanes*) as wellas S.C (*Saccharomyces cerevisiae*) whereas the samples V-3 and V-4 shows the inhibition of 5mm against S.C and colony diameter of fungus well decreases. Such activity of metal complexes could be due to the fact that lipid membrane that surrounds the cell favors passage of only lipid soluble material which control the antimicrobial activity²³⁻²⁴. It is also because of the fact that chromium(III) porphyrin complexes are found to be used in plasma treatment²⁵.

4. Conclusion

On the basis of above elemental analysis and spectrochemical studies a monomeric octahedral structure is proposed for these complexes. Definite crystal structure could obtained by X-ray crystallography which is under process. The biological activity of complexes shows that they have prominent antifungal activity but exhibit negligible antibacterial and antioxidant behaviour.

Com- pound	Antibacterial study							Antifungal study		
	B.C	M.L	S.A	P.A	S.P	B.S	K.P	L.C	C.A	S.C
V-1										
V-2									8mm	8mm
V-3										5mm
V-4										5mm

So μ l of stock of 1mg/ml was added into the well.

The dotted line show no activity present

S.A = Stephylococcusaureus	E.C = Esclerischia coli
M.L = Micrococcusluteus	K.P = Klebsiella pneumonia
B.S = Bacillus subtilis	S.C = Saccharomyces cer- evisiae
B.C = Bacillus cereus	C.A = Candida albicans

P.A = Pseudomonas aeruginosa

S.P = streptococcus pyogenes

REFERENCE 1. Eberhard U. M, in "Transport by Portein", Ed. By Blaner. G. and Sund. H., Walter deGruyter and Co., Berlin, 1978, 295. | 2. Calvin M., Acc. Chem. Res., 1978, 11(12), 474-474. | 3. Bonnet R., Chem. Soc. Rev., 1995, 24, 19-33. | 4. North J., Neyndroff H. and Levy J.G., J. Photochem. Photobiol. B: Biol., 1993, 17(2), 99-108. | 5. Papazoglou T. G., J. Photochem. Photobiol. B: Biol., 1995, 28(1), 3-11. | 6. Jori G., Perria C., Eds. Photodynamic Threapy of Tumors and other diseases, LibreriaProgetto, Editore via Marzolo, Padova, Italy. 1985, 311-316. | 7. Henderson B., Doughtery T., Eds. Photodynamic Threapy, Basic of Tumors and other diseases, LibreriaProgetto, Editore via Marzolo, Padova, Italy.1985, 311-316. [7. Henderson B., Doughtery T., Eds. Photodynamic Threapy, Basic Principles and Clinical Applications, Marcel Dekker, New York. 1992, 219-268. [8. Hamor G. H and Watson D., J. Pharmaceutical Science, 2006, 60(6), 925-927. [9. Hein D. W., Alheim R. J. and Leavitt J. J. J. Am. Chem. Soc., 1957, 79(2), 427-429. [10. Attog F. A. A., Journal of Chemistry, 2009, 6(1), 281-288. [11. Sumuel T., David K. D., Regina A. and Isacc T., J.Inorg. Chem., volume 2014, Article ID 586131. [12. Al-Amiry A.A, Kadhum A. A and Mohammed A. B., volume 2012, Article ID 795812. [13. Choudhary A., Sharma R., Nagar M., Mohsin M. and Meena H. S., J. Chilean Chem. Soc., 2011, 56(4), 911-917. [14. Oke-F, AslimB, Ozturk S. and Altumday S., Food chemistry, 2009, 112(4), 874-879. [15. Longo A.D., Longo F.R, Finarelli J.D., Goldmcker. J., Assour J. and Korsakoff L., J.Inorg. Chem. 1967, 32(2), 476-476. [16. Buchler J. W., Puppe L., Rhbock K. and Schneehage H. H., Ann N. Y., Acad. Sci., 1973, 206, 116 [17. Eisner U. and Harding M. J. C., J. Chem. Soc., 1964, 4089-4101. [18. Mehrotra R. C. and Singh J., Inorg. Chem., 1984, 23(8), 1046-1048. [19. Gouterman M., Hanson L. K., Khalil G. E., Leenstra W. R. and Buchler J. W., J. Chem. Phys., 1975, 62(6), 2343-2353. [20. Burger H., Spectroscopy inPorphyrins and Metallorphyrins, Smith H.E., ed, 525-538, Elsevier, Amsterdam, chapter 11. [21. Silverstein R. M., Bassler G. C., Morrill T. C., Spectrometric identification of organic compounds, John Wiley and Sons. Inc., New York, Ed. 39, 1974 [22. Nakamoto K., Infrared and Raman spectra of inoraanic and co-ordination compounds, John Wiley and Sons. Inc., New York, Ed. 39, 1974 [22. Nakamoto K., Infrared and Raman spectra of inoraanic and co-ordination compounds, John Wiley and Sons. Inc., New York, Ed. 39, 1974 [22. Nakamoto K., Infrared and Raman spectra of inoraanic and co-ordination compounds, John Wiley and Sons. Inc., New York, Ed. 39, 1974 [22. Naka Infrared and Raman spectra of inorganic and co-ordination compounds, John Wiley and SonsInc., New York, Ed. 5, 1997. | 23. Vincent J. M., Nature, 1947, 159, 850. | 24. Dharmaraj N., Viswanathamurthi P. and Natarajan K., Trans. Met. Chem., 2001, 26(1-2), 105-109. | 25. HeierP., BoscherN. D., Bohn T., HeinzeK. and ChoquetP., J. Mater. Chem. A, 2014, 2, 1560-1570.