



Synthesis and Characterization of Metal(II) Phthalocyanine Containing N,N-dimethyl Phenyl Moieties

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ABSTRACT

Synthesized of novel metal (II)-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanines (MTDMPHmPc) [M=Co, Ni, Cu, Zn] by an effective and suitable method. The tetra-nitrophthalocyanines converted into aminophthalocyanines by reduction. Than amino phthalocyanines derivatives bearing tetra-4-(N,N-dimethyl phenyl) to form tetra substituted 4-(N,N-dimethyl phenyl) methane-imine phthalocyanines complexes. These derivatives compounds were characterized by FTIR, elemental analysis, magnetic and powder XRD properties to check the purity and structural integrity. Magnetic measurements on copper and cobalt substituted phthalocyanine complexes in the range of magnetic strength 2.21 to 4.02 kG that a variation of field strength with magnetic moments due to the presence of an intermolecular cooperative effect.

Keywords: Phthalocyanine, Tetra-4-(N,N-dimethyl phenyl) methanimine, FTIR, Electronic, XRD, Magnetic susceptibility, Thermogravimetric analysis.

INTRODUCTION

Phthalocyanines are heteroaromatic macrocyclic compounds. It is accidental investigated in 1928, the blue and green colour pigments¹. Phthalocyanines are more versatility and highly stable complexes due to more than seventy (70) transitional non-metallic and metallic ions substituted in the ring cavity². Phthalocyanines applications such as dyes and pigments³, in photovoltaic cells⁴⁻⁵, photodynamic therapy⁶, semiconductor materials⁷, as liquid crystals⁸⁻⁹, LED¹⁰, optical storage devices¹¹, moletronics¹², non-linear optical¹³, gas sensors¹⁴,

and for electrochromic displays¹⁵. The reduction-oxidation properties of phthalocyanines are use as industrial applications like dyes and pigments¹⁶. To modify these macrocyclic compounds have been performed advanced materials for numerous properties and applications.

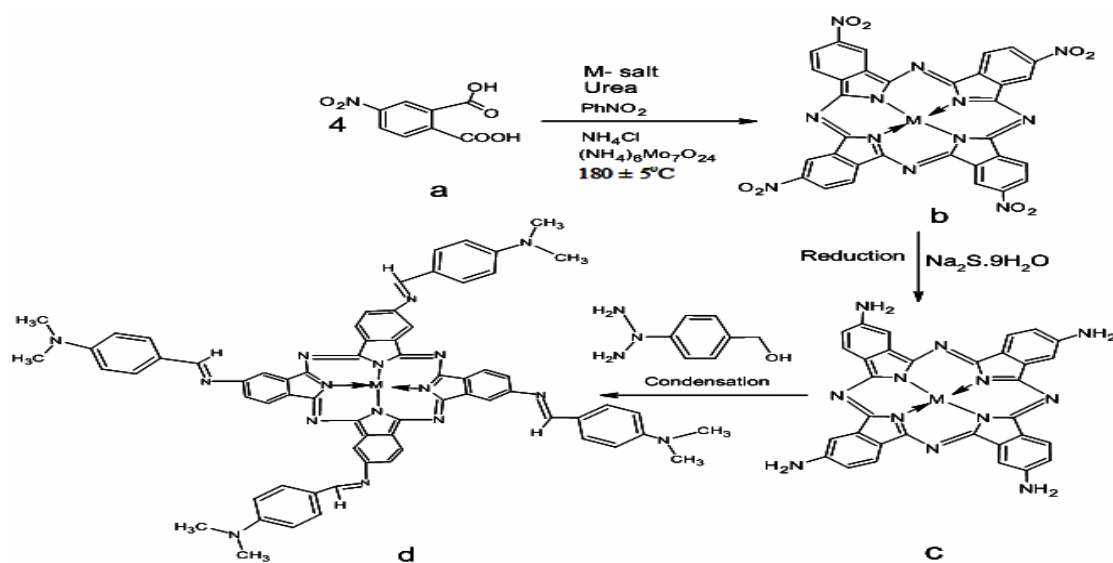
Phthalocyanines are partially soluble in organic solvents like CCl₄, acetone or in H₂O. These insolubility due to peripheral substitution with long alkyl, alkylthio chain, alkoxy, and bulky groups lead to macrocyclic products. Phthalocyanines are soluble in a polar solvent.



In this work, we attempt has been made to synthesize and characterization of a non-peripherally metal(II) phthalocyanine presence of tetra substituents of (N,N-dimethyl phenyl) methan-imine molecule. The amino phthalocyanines complexes react with substituted aldehydes compounds to form imine group. Even though, literature papers revealed the reports on the synthesis and characterization of substituted metal(II) tetra-amino phthalocyanines,

no documentary pieces of evidence were available on the newly synthesis and characterization of substituted metal-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanine pigments.

This paper concerns suitable synthetic route available in the literature and modified the procedure the synthesis of metal (II)-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanines in Scheme 1.



Scheme. 1. Synthetic route of metal (II) tetra-4-(N,N-dimethyl phenyl) methane-imine phthalocyanine pigments.
a. 4-nitro-phthalic acid, b. MTNPc c. MTAPc d. MTDMPHmPc

MATERIALS AND METHODS

The carbon, hydrogen and nitrogen analysis carried out by the Sophisticated Test and Instrumentation Centre at Cochin University, Kochi, India. The FTIR spectra were recorded on a Nicolet MX-FTIR spectrometer using KBr pellets. Magnetic susceptibility studies by using a Gouy balance and at room temperature (301°K). Diamagnetic corrections is calculate were used Pascal's constants¹⁸⁻¹⁹. A calibrant used as a mercury tetra thiocyanato cobalt(II) complex and doubly distilled H₂O was used in the experiments. Electronic spectra on a UV-Vis Shimadzu 3600 UV-spectrophotometers. Rigaku Miniflex 600 XRD diffractometer was used to measure the diffraction pattern. Thermogravimetric and DTA analysis is carried out by using Perkin- Elmer Thermal analyzer at the rate of 10°C/min in air and nitrogen atmosphere.

EXPERIMENTAL

4-nitrophthalic acid was prepared as per literature¹⁹ and other solvents and reagents used were analytical grade. The substituted metal(II) tetra-nitro phthalocyanines and metal(II) tetra-aminophthalocyanines were prepared by the reported procedure¹⁹. These complexes converted into imino substituted complexes by condensation reaction²⁰. Finally we prepared metal (II)-4-(N,N-dimethyl phenyl) methan-imine phthalocyanines complexes and synthesized compound analytical data were summarized in the table.

Preparation of Cobalt (II)- tetra-4- (N, N-dimethyl phenyl) methan-imine phthalocyanine complex

Cobalt(II) tetra-aminophthalocyanine (6.31g,/0.1mole) were 15 M H₂SO₄ added successively, 4-dimethylamino benzaldehyde (14.9g,/0.1mole) was dissolved in ethanol and a

small amount of concentrated H₂SO₄ was added, and refluxed 5 h with constant stirring²⁰. The blue-colored condensed tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanine derivative and washed with ethanol until its free from substituted aldehyde and collect pure product. Finally, washed with dis. H₂O and product was dried vacuum desiccator over anhydrous O₁₀P₄.

The above same procedure adopted the preparation of Cu, Ni, and Zn -tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanines.

RESULTS AND DISCUSSION

All the substituted metal(II) phthalocyanines are bluish color. The metal phthalocyanine complexes are soluble in concentrated sulfuric acid and sparingly soluble in dimethyl sulfoxide, and Dimethylformamide and pyridine. The solubility increasing order like sulfuric acid > dimethyl

sulfoxide > Dimethylformamide > pyridine. The elementary analysis C, H, and N result summarized in Table 1 and calculated values with consistent by the suggested structure (Figure 1).

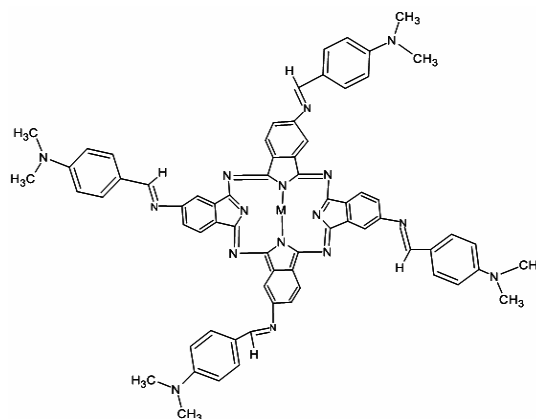


Fig. 1. Proposed structure of metal(II)-tetra-4-(N,N-dimethyl phenyl) methanimine phthalocyanines, where (M=Cu, Co, Ni, Zn)

Table 1: Magnetic susceptibility and elemental analyse data of metal (II)- tetra-4-(N,N-dimethyl phenyl) methanimine phthalocyanine

Name of the Complex [Colour] (% Yield)	Molecular formulae. (Molecular weight)	Field KGauss	Magnetic susceptibility $\chi_m \times 10^{-6}$	Magnetic moments μ_{eff} [BM]	Elemental analysis [%] [found (calcd)]
CoTDMPHmPc 75% [Dark Blue]	C ₆₈ H ₅₆ N ₁₆ Co -1156.2	2.21	2611.13	2.64	C, 70.58; (70.45) H, 4.84; (4.79) N, 19.37; (19.27) Co, 5.09; (5.05)
		2.63	2434.05	2.46	
		3.1	2114.43	2.28	
		3.57	1929.02	2.17	
		4.02	1808.03	2.13	
CuTDMPHmPc 74% [Dark Blue]	C ₆₈ H ₅₆ N ₁₆ Cu -1160.81	2.21	2621.08	2.58	C, 70.34; (70.33) H, 4.82; (4.77) N, 19.31; (19.23) Cu, 5.47; (5.45)
		2.63	2465.17	2.46	
		3.1	2128.43	2.28	
		3.57	1947.55	2.18	
		4.02	1825.54	2.13	
NiTDMPHmPc 70% [Dark Blue]	C ₆₈ H ₅₆ N ₁₆ Ni -1155.96	2.63	-773.81	---	C, 70.59; (70.56) H, 4.84; (4.79) N, 19.37; (19.33) Ni, 5.07; (5.02)
ZnTDMPHmPc 70% [Dark Blue]	C ₆₈ H ₅₆ N ₁₆ Zn -1162.65	2.63	-1239.03	---	C, 70.18; (70.14) H, 4.81; (4.78) N, 19.26; (19.23) Zn, 5.62; (5.59)

Electronic spectra (UV-Visible)

The metal(II)-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanine complex

(M-TDMPHmPc) were performed concentration range 1-1.5 X 10⁻⁴ M in dimethyl sulfoxide and the data are presented in Table 2. The peaks were shown

in the range of 774-784 for all the complexes due to $a_{2u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$ transition²⁰. The Q-band M-TDMPHImPc's was found compared to higher corresponding parent substituted metal(II) phthalocyanines. The lower energy redshift band is due to extension in the $\pi-\pi^*$ transition electron of peripheral substitution of aromatic component

imino group. CoTDMPHImPc, CuTDMPHImPc, NiTDMPHImPc and ZnTDMPHImPc absorption peak were shown in the range of 686-691nm which indicate for attributed to the phthalocyanine complexes²¹. B-band and L-band was observed in the range of 242-249nm and 206-217nm for all the complexes.

Table 2: UV-Visible, Infra-red and X-ray diffraction spectral data of metal(II)-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanine complexes

Name of the Complex	UV-Vis absorption λ_{nm} [log ϵ]	IR spectral data [cm^{-1}]	Powder XRD $2\theta(o)$ (d Å)	Relative Intensity (%)
CoTDMPHImPc	206 (3.42)	741, 1040, 1175,	27.87, (3.49)	100
	242 (3.59)	1386, 1633, 1708,	28.73, (3.08)	79.34
	481 (3.24)	2364, 3450.	24.47, (3.42)	49.16
	691 (4.32)		31.23, (2.83)	31.54
	784 (3.82)			
CuTDMPHImPc	209 (3.33)	773,1091, 1387,	45.54, (2.82)	100
	257 (4.19)	1632, 1712, 2363,	31.72, (2.80)	80.23
	478 (3.87)	3442.	43.73, (2.74)	50.47
	688 (4.15)		25.93, (3.42)	33.35
	776 (3.17)			
NiTDMPHImPc	212 (3.49)	756, 1113, 1366,	27.81, (3.74)	100
	257 (4.15)	1404, 1624, 2223,	28.83, (3.08)	79.78
	479 (3.41)	2361, 3423.	23.24, (3.43)	44.15
	686 (4.54)		42.77, (2.80)	28.58
	774 (3.64)			
ZnTDMPHImPc	217 (3.59)	771, 1121, 1387,	27.93, (3.57)	100
	259 (4.47)	1633,2324, 2363,	28.87, (3.06)	80.87
	471 (3.59)	3445.	42.93, (2.81)	50.15
	689 (4.24)		20.52, (4.30)	35.93
	779 (4.57)			

Infra-red

The Infra-red spectral data of the metal (II)-tetra-4-(N,N-dimethyl phenyl) methanimine phthalocyanines are presented in Table 2 (Fig. 2). A peak is assigned in the range of 3422-3442 cm^{-1} in all the complexes due to H-bonding between the hydrogen atom of moisture observed on the KBr pellets and the nitrogen atom of the phthalocyanine skeleton²². A sharp is observed in the range of 1624-1633 cm^{-1} are assigned to C=N bond of the imine group. The peaks in the range of 1367-1386 cm^{-1} are attributed to C-N bond aromatic stretching¹⁸. A weak peak at 2359-2367 cm^{-1} are assigned to C-H stretching vibration due to phthalocyanine moiety. All the peaks at 1040-1121 and 745-776 cm^{-1} can be attributed to the various characteristic phthalocyanine ring stretching skeletons²².

Magnetic Susceptibility Measurement

The synthesized M-TDMPHImPc's complexes are measure the magnetic susceptibility

were solid state and summarized the results in Table 1. The measurement of applied magnetic field in the range of 2.21 to 4.02 kG and independent determination by average of three values.

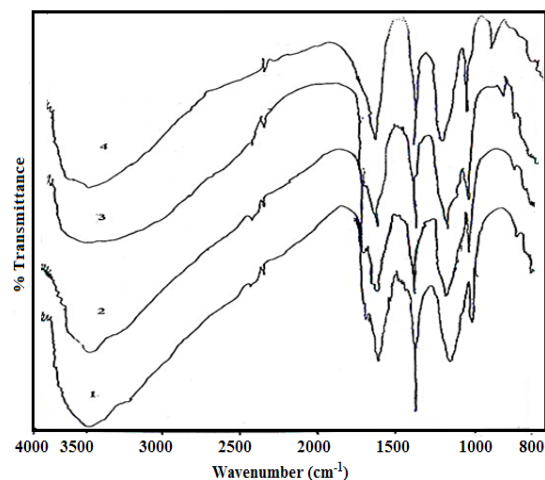


Fig. 2. Infrared absorption spectra of (1) CuTDMPHImPc (2) CoTDMPHImPc (3) NiTDMPHImPc (4) ZnTDMPHImPc

While copper and CoTDMPHmPc are paramagnetic behavior and NiTDMPHmPc, ZnTDMPHmPc complexes are diamagnetic nature. The magnetic moments of CuTDMPHmPc and CoTDMPHmPc are higher values than the spin-spin only value corresponding to the one unpaired electron 1.73BM, due to the blending of higher energy state ($b_{2g/2}$, $e_{g/3}$, $a_{1g/2}$) orbital with ground state ($b_{2g/2}$, $e_{g/4}$, $a_{1g/1}$) orbitals degenerate states and inter-molecular cooperative effect²³. As per the literature the magnetic field is higher than the higher magnetic moment values at lower field strength due to magnetic anisotropy of phthalocyanine coupled with intermolecular magnetic interaction¹⁷⁻²⁰.

Powder X-ray Diffraction

The powder XRD pattern of MTDMPhmPc's are taken in the range of 2θ angle 06-70° and it was observed that all the peaks are identical data is reported in the Table 2. In the spectra one of the

sharp peak is observed maximum intensity with lower angle. The following values of interplanar spacing with angle. Co-TDMPHmPc 3.54, 27.87 Å; Cu-TDMPHmPc 2.78, 45.62 Å; Ni-TDMPHmPc 3.64, 27.92 Å and Zn-TDMPHmPc 3.55, 27.91 Å, It is clearly indicating these complexes are crystalline nature. A similar pattern is observed in un-substituted parent phthalocyanine complexes. The broadening of the peaks in the MTDMPhmPc's due to the attributed of the substituents group and play an important role in stacking the substituted metal (II) phthalocyanine complexes²⁴.

Thermogravimetric studies

Thermogravimetric analytical data of metal(II)-tetra-4-(N,N-dimethyl phenyl) methanimine phthalocyanine pigment reported in Table 3 and 4. In these complexes the decomposition take place in 2 steps. Initially weight loss of complexes 2-3% due to moisture.

Table 3: Thermogravimetric analysis data of metal(II)-tetra-4-(N,N-dimethyl phenyl) methanimine phthalocyanine

Complex	Decomposition Temperature (°C)	Weight Loss (%)found	Weight Loss (%)calcd	Probable fragmentation loss
CuTDMPHmPc	240-350	28.74	29.03	4-substituted imino groups
	351-620	64.56	64.92	Pc- moiety
CoTDMPHmPc	240-350	29.92	30.14	4-substituted imino groups
	351-620	65.86	65.03	Pc -moiety
NiTDMPHmPc	240-350	28.78	29.17	4-substituted imino groups
	351-620	64.16	64.78	Pc- moiety
ZnTDMPHmPc	240-350	29.65	30.12	4-substituted imino groups
	351-620	65.53	65.13	Pc -moiety

Table 4: Thermodynamic and kinetic parameters of tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanines complexes in air and nitrogen

Complex		Activation energy, E _o kJ/(mol)	Frequency) factor. (lnA)	ΔH kJ/(mol)	ΔS J/K	ΔGkJ/(mol)
CuTDMPHmPc	I	5.86 (0.72)	6.17 (2.02)	2.73 (-1.28)	-165.05 (-160.02)	62.41 (61.53)
	II	3.73 (1.52)	5.37 (5.45)	-0.74 (-2.42)	-152.26 (-149.74)	81.64 (79.53)
CoTDMPHmPc	I	0.87 (0.65)	6.38 (3.37)	-1.27 (-1.13)	-175.07 (-173.12)	73.94 (73.76)
	II	4.67 (1.15)	7.40 (4.55)	2.86 (-1.22)	-143.93 (-140.98)	79.55 (76.23)
NiTDMPHmPc	I	1.46 (0.72)	5.23 (2.17)	-1.23 (-0.75)	-158.56 (-156.57)	72.85 (71.57)
	II	5.86 (1.55)	4.46 (4.80)	-0.84 (-0.81)	-148.78 (-142.64)	81.74 (79.98)
NiTDMPHmPc	I	1.74 (0.69)	3.47 (2.35)	-0.94 (-1.43)	-174.86 (-172.36)	74.23 (73.97)
	II	8.53 (5.52)	7.86 (6.35)	2.85 (-1.54)	-141.73 (-139.92)	81.47 (79.94)

The values I and II stage represent the degradation in nitrogen atmosphere.

1st step of degradation the temperature ranges from 240-350°C, in air, the loss of all the four substituted imino groups. In second step the temperature ranges 351–620°C maximum weight loss is identified in all the phthalocyanines complexes due to the oxidative degradation in the phthalocyanine moiety. Destruction of phthalocyanine complexes only in the second step. Finally, the remaining residue corresponds to metal oxide²³.

The metal(II)-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanine complexes are thermally decomposition take place very slow in nitrogen atmosphere. For CoTDMPHmPc was decomposed 68% at temperature 620°C. For CuTDMPHmPc, 55%, NiTDMPHmPc, 53% and ZnTDMPHmPc complexes 44% loss of weight at temperature 620°C. From the result it is conclude that the thermal stabilities of these MTDMPHmPc in the order. CoTDMPHmPc>CuTDMPHmPc>NiTDMPHmPc>ZnTDMPHmPc. Thermodynamic and kinetic studies of the metal(II)-tetra-4-(N,N-dimethyl phenyl) methan-imine phthalocyanine complexes were evaluated by Boride's method²⁵. (Figure 3).

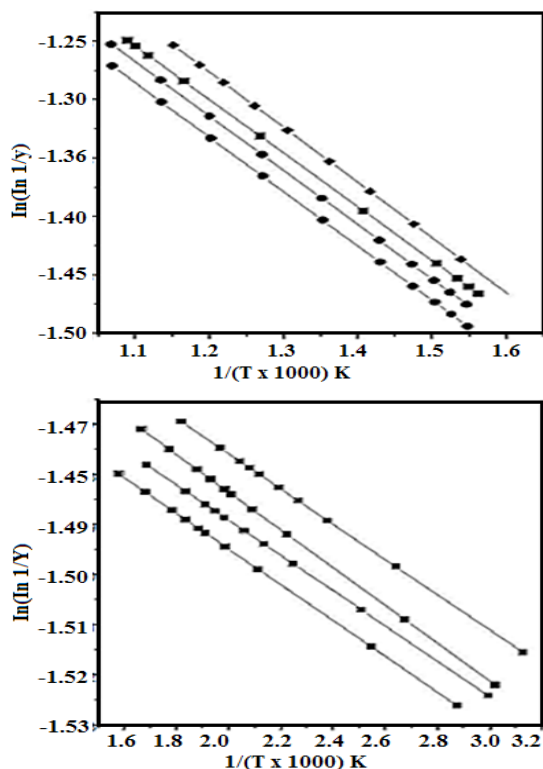


Fig. 3. Thermal degradation $\ln(\ln 1/y)$ v/s $1/T$. CuTDMPHmPc, CoTDMPHmPc, NiTDMPHmPc and ZnTDMPHmPc in atm.air

Plot of graph $\ln(1/y)$ v/s $1/T$. The activation energies (E_0), for the loss of periphery imino substituent groups in all the complexes lies in the range of 0.69–5.86 kJ/ (mol) due to the periphery substituents groups are removed, and the disrupt of the phthalocyanines complex ring. It is exothermic reaction the negative entropies and the degradations are completed. The changes in entropies ΔS varies from -158.56 to -174.86 kJ due to this result it is indicated that all functional groups are associated with negative entropies. The enthalpy, entropy and free energy have been calculated by using standard equations and results are summarized in Table 4.

CONCLUSION

The synthesized of metal(II)-tetra-4-(N,N-dimethyl phenyl) methanimine phthalocyanine substituted different transitional metal like (Cu, Co, Ni and Zn) by simple method and characterized. All the complexes the solubility increased in organic solvents due to introduce of (N,N-dimethyl phenyl) group into periphery positions of metal phthalocyanine. Macrocyclic compounds solubility increases the research community are potential applications in different field like sensor, catalysts, electrode coating and pharmaceutical industries. The magnetic susceptibility studies confirm that CuTDMPHmPc and CoTDMPHmPc are paramagnetic nature. XRD studies revealed that crystalline nature of the complex. The thermal stability of the metal(II) TDMPHmPc's in air, the following order CuTDMPHmPc>CoTDMPHmPc>NiTDMPHmPc>ZnTDMPHmPc.

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Conflicts of Interest

All author declare that there is no conflict of interest.

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