



Synthesis and Spectral Studies on Substituted Metal (II)-Tetra-1-(Thiophene-2-yl)methanimine Phthalocyanine Complexes

FASIULLA*¹ and YASHODA. M. P.¹

¹Department of Chemistry, Manipal Institute of Technology, MAHE, Manipal, Udupi District, Karnataka, India.

*Corresponding author E-mail: fasiulla1976@gmail.com

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ABSTRACT

The synthesis, characterization of symmetrically substituted transition metal (II)-tetra-1-(thiophene-2-yl) methaniminephthalocyanine complexes by condensation of tetraamino phthalocyanines with 2-thiophenecarboxaldehyde had been prepared. The structural and characterization of the blue colour tetra -1-(thiophene-2-yl)methanimine phthalocyanine complexes are elucidated by using a number of analytical techniques like FT-Infrared, UV-Vis spectroscopy, XRD, magnetic measurements and thermo-gravimetric analysis. The kinetic parameters and thermal decomposition of synthesized phthalocyanines complexes were calculated using thermo-gravimetric analytical data.

Keywords: Tetra-(thiophene-2-yl) methanimine, IR spectra, Magnetic measurements, X-ray powder diffraction, TGA.

INTRODUCTION

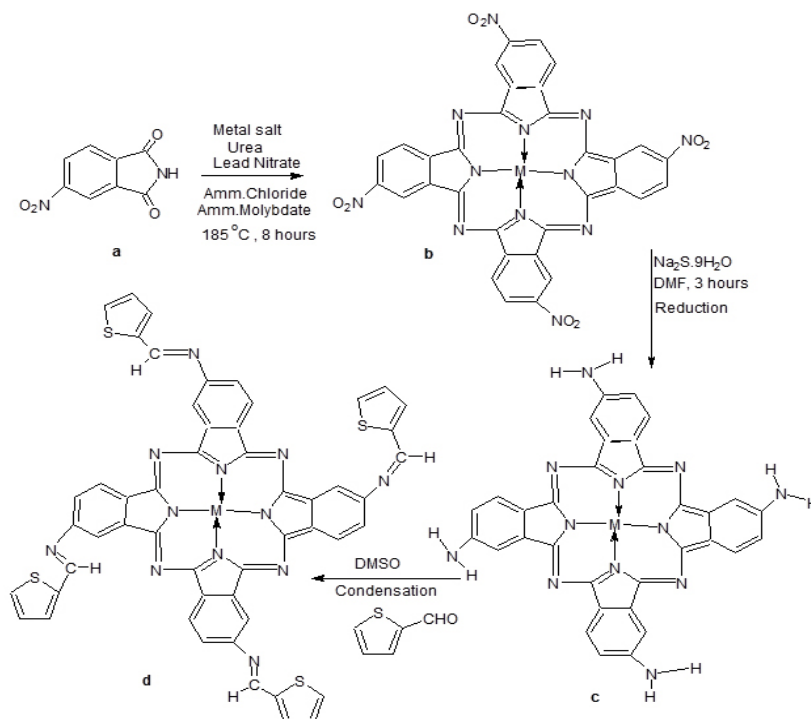
As the metal phthalocyanines were prominent as dyes and pigments, so the first and foremost interest was taken in them. Phthalocyanines are commercial blue-green coloured pigments too. The blue-green colour is the result of strong absorption in the Q-band, the visible region of the spectrum. The succeeded intensive research is aimed at proving into, how the produce of the phthalocyanines was used sensitizers in photodynamic therapy and

other medical applications and phthalocyanine derivatives are known for their applications in the field of liquid crystals, semiconductor devices, electro-photography, molecular electronics, electro-catalytic reagents, and also in the field of opto-electronics, electronics, and photonics. Solubility and varied physico-chemical properties related with metal phthalocyanines were primarily depended upon the central metal atom, as well as the molecule's peripheral position.



In this paper we have discussed the synthesis, spectral, magnetic susceptibility on symmetrically substituted transition metal (II) tetra-(thiophene-2-yl) methanimine phthalocyanines. The available procedure is relatively modified and used for the

synthetic route in the literature. The substituted transition metal (II) tetra-1-(thiophene-2-yl) methanimine phthalocyanine complexes is given as per the scheme-1.



Scheme 1. Synthesis of 2, 9, 16, 23- tetra-1-(thiophene-2-yl) methanimine phthalocyanines.
a. 4-Nitrophthalimide b. MPcON c. MPcOA d. MTTImPc

EXPERIMENTAL

4-Nitrophthalimide were procured from Sigma-Aldrich. All the other chemicals were purchase from different chemical supplier. The substituted transition metal (II) tetraamino phthalocyanines complexes condensed into iminophthalocyanine complexes with 2-thiophenecarboxaldehyde compounds as shown in scheme-1.

Synthesis of Cobalt (II) tetra-1-(thiophene-2-yl) methaniminephthalocyaninecomplex

4-nitro phthalamide (1 eq), cobalt sulphate (0.26 eq), and ammonium molybdate (0.5 eq) were taken with 12 mL of nitrobenzene, catalytic amount of ammonium molybdate and excess of urea in 3 necked round bottom flask. Reaction was kept for 120 °C for first one hour and then gradually increased the temperature for every 30 min., and finally, the mixture was heated to maintain 180 °C for 5 h to form tetranitro cobalt phthalocyanine.

In the next step thus formed Tetra nitro cobalt phthalocyanine (1 g eq.) and (8 g eq.) of sodium sulfide were taken with dimethyl formamide in a 100 ml round bottomed flask and kept for stirring at 80 °C for 24 hours. The mixture was poured into ice cold water and the precipitate was formed, filtered off and washed with hot water several times to remove unreacted sodium sulfide. Then it was given a 0.1N HCl wash several times followed by washing repeatedly with 0.1N NaOH. Finally the precipitate is washed with hot H₂O, filtered and dry in oven.

The finely powdered cobalt(II) tetraamino phthalocyanine (M-PcTA) (6.32 g 0.01 mole) was dissolved in dimethyl sulfoxide with stoichiometric ratio of 2-thiophenecarboxaldehyde (12.6 mL, 0.01 mole). In the catalytic quantity of conc.H₂SO₄ the mixture got refluxed for 5 hours. Then mixture were poured in to an ice-cold water. The precipitate was washed with alcohol until several times to formed

completely free from substituted aldehydes. The precipitate is washed with distilled hot water and dried in vacuum P_2O_5 . Similar procedure is adopted to prepared the CuTTImPc, NiTTImPc, ZnTTImPc complexes.

METHODS

Elemental analysis was carried out at STIC, Kochi, Kerala, India. The Gouy magnetic balance was used to measure the magnetic susceptibility of tetra substituted metal (II) iminomethane phthalocyanines at room temperature. Mercury cobalt(II) tetrathiocynaide as calibrant used reference complex to calculate diamagnetic behavior. Shimadzu UV-Visible spectrometer, UV-160A used for recording electronic absorption spectra. FT-IR spectral was used to identify the different functional groups in compounds. The diffraction patterns was recorded by using Phillip PW1710 XRD. Perkin Elmer thermal analyzer at a heating rate of $10^\circ/\text{min.}$, both in the nitrogen atmosphere and air to calculate the TGA data.

RESULTS AND DISCUSSION

Tetra-1-(thiophene-2-yl) methanimine phthalocyanines complexes are synthesis by adopting simple modified procedure. The colour of the complexes is bluish green in nature. It is soluble in DMF, DMSO, conc. H_2SO_4 , pyridine and partially soluble in ethanol. The percentage of carbon, hydrogen, nitrogen, sulphur are agreed with theoretical value indicating the purity of the synthesized complexes. The proposed structure of the synthesized Tetra-1-(thiophene-2-yl) methanimine phthalocyanines complexes are shown in scheme-1 and Figure 1.

Electronic [UV-Visible]

The concentration range at $1.0-1.5 \times 10^{-4}$ M in DMF, the electronic spectra of M-TTImPcs was recorded Fig. 2 and Table 1. The bluish color of the phthalocyanine compound observed due to a_2u_{eg} & b_2u_{eg} transitions state. The corresponding parent metal phthalocyanines are lower than the all complexes shows in the wavelength range 721-734 nm. In all the complexes Q-band was doubled by ranging 572-588 nm. And the a_1u_{eg} transition state of the phthalocyanine moiety was attributed with the originated Q-band both the sharp intense B-band

ranged 325- 332 nm and weak L-band ranged 211- 219 nm was observed for all the complexes these B-band and L-band may be accounted for C-band in the phthalocyanines moiety.

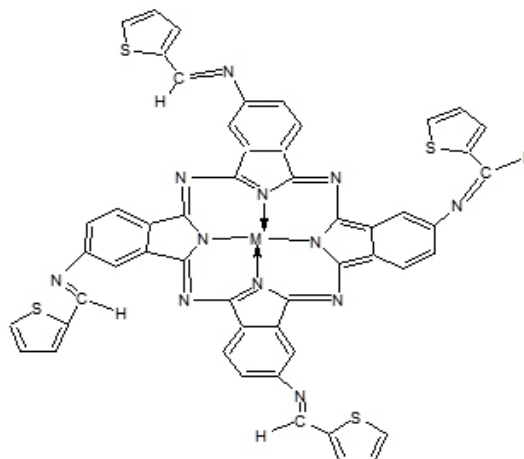


Fig. 1. Proposed structure of substituted metal (II) 2,9,16,23-(thiophene-2-yl) methanimine phthalocyanine complexes. M=[Cobalt, Copper, Nickel, Zinc]salts

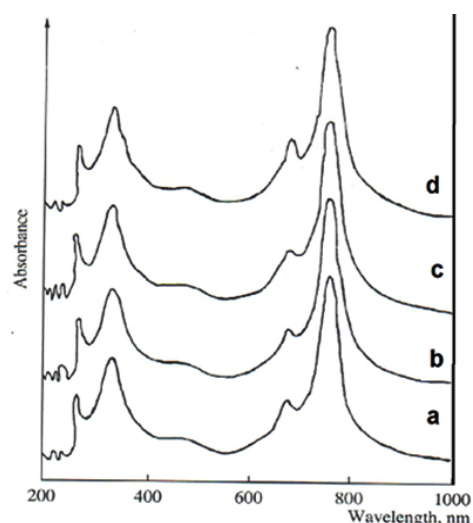


Fig. 2. Electronic Spectra of a) CoTTImPc, b) Cu-TTImPc, c) Ni-TTImPc, d) Zn-TTImPc

Infra-red

Relevant Infra-red data was recorded by using KBr pellets, results are reported in Table 1, Fig. 3. An intense (sharp) peak in the range $1619-1630\text{ cm}^{-1}$ is due to C=N of imine group. C-N Ar. stretching vibration peak in the range of $1365-1388\text{ cm}^{-1}$. The C-S-C asy. stretching vibration

is assigned in the range of 768 – 643 cm^{-1} and C-S-C sym. stretching vibrations is observed in the range 1058- 1118 cm^{-1} . The peak is assigned in the range 3424- 3450 cm^{-1} hydrogen bonding due to nitrogen

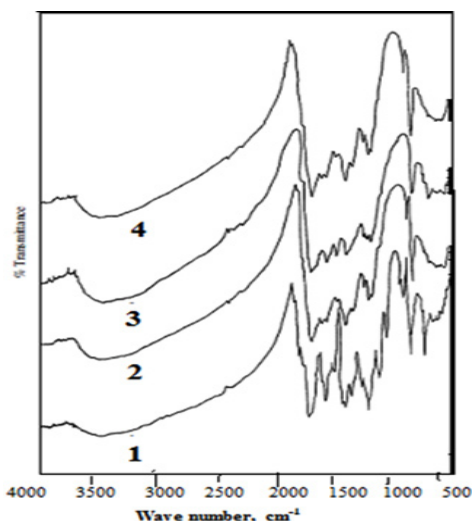


Fig. 3. IR spectra of 1) Co-TTImPc, 2)Cu-TTImPc,3) Ni-TTImPc, 4) Zn-TTImPc

atom in the phthalocyanines moiety and hydrogen atom in the KBr pellets. A weak signal C-H vibrational stretching at the periphery of the phthalocyanines moiety is assigned at the range 2325-2366 cm^{-1} . The range of 551-590 cm^{-1} are attributed to various characteristic skeletal peak of the phthalocyanines molecule

Magnetic susceptibility

At an ambient temperature, magnetic measurement data are presented in Table 2. As per the magnetic measurement studies CuTTImPc, CoTTImPc are behaves as paramagnetic complexes and like wise NiTTImPc, ZnTTImPc are diamagnetic complexes in nature. The magnetic moment measured are higher the spin value in CuTTImPc and CoTTImPc compare to corresponding unpaired electron. By the crystallographic studies substituted phthalocyanines different metal are isomorphous and have sq. planar structure with D_{4h} symmetry in Figure 4.

Table 1: Electronic and IR spectra data

Complex Name Yield (%) (Colour)	Molecular formula (Molecular weight)	UV-visible absorption λ nm (log ϵ)	Elemental analysis (%) found (calcd)	IR-Spectral Data (cm^{-1})
Co-TTImPc -85% (Dark green)	$\text{C}_{52}\text{H}_{28}\text{N}_{12}\text{S}_4\text{Co}$ -1006.93	215 (4.90) 264 (4.79) 328 (5.39) 588 (5.07) 734 (5.11)	C, 61.90; (61.97) H, 2.68; (2.78) N, 16.54; (16.68) S, 12.67; (12.71) Co (5.85)	590, 768, 1058, 1124, 1378, 1619, 1709, 2366, 3450.
Cu-TTImPc -84% (Dark green)	$\text{C}_{52}\text{H}_{28}\text{N}_{12}\text{S}_4\text{Cu}$ -1011.55	211 (4.87) 259 (4.76) 332 (5.40) 577 (5.01) 732 (5.12)	C, 61.54; (61.68) H, 2.67; (2.76) N, 16.53; (16.60) S, 12.60; (12.65) Cu (6.28)	582, 670, 1090, 1385, 1630, 1714, 2365, 3442.
Ni-TTImPc -83% (Dark green)	$\text{C}_{52}\text{H}_{28}\text{N}_{12}\text{S}_4\text{Ni}$ -1006.69	214 (4.78) 262 (4.59) 325 (5.02) 580 (4.52) 724 (4.59)	C, 61.91; (61.98) H, 2.70; (2.78) N, 16.62; (16.68) S, 12.68; (12.71) Ni (5.82)	573, 663, 1112, 1365, 1402, 1626, 2221, 2360, 3424.
Zn-TTImPc -80% (Dark green)	$\text{C}_{52}\text{H}_{28}\text{N}_{12}\text{S}_4\text{Zn}$ -1013.39	219 (5.21) 251 (5.40) 330 (5.47) 572 (5.39) 721 (5.04)	C, 61.54; (61.57) H, 2.71; (2.76) N, 16.52; (16.57) S, 12.60; (12.63) Zn (6.45)	551, 643, 1118, 1388, 1627, 2325, 2362, 3441.

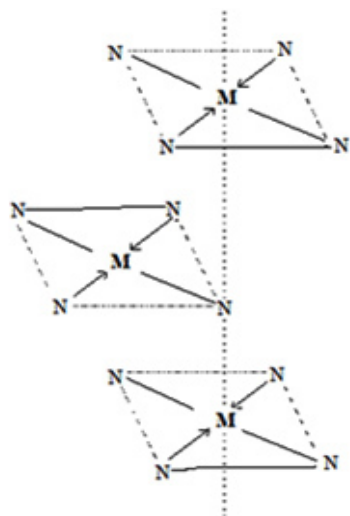


Fig. 4. Mechanism of molecular stacking of metal phthalocyanine crystal, (M = Cu(II), Co(II), Ni(II), Zn(II))N= azamethaine atom

Powder XRD

The range of 2° angles were used take the powder XRD pattern of MTTImPcs. Angles 6-70° showed the relatively very poor crystalline peaks Table 2. The pattern is observed to same as the unsubstituted phthalocyanine complexes except the

peak with diffuse intensity. Because of the molecular periphery there was a broadening in pattern. This broadening gives the hindrance due to effective stacking of the molecule. It is poor crystalline in nature phthalocyanine complexes.

Thermogravimetric and kinetic studies

In the Table 3, the thermo gravimetric analysis data are reported. In the two steps, an occurrence of the decomposition of above complexes was found. The first step indicated all the substituent groups in phthalocyanines are degradation in air at the temperature 250 to 350 °C. In the second step degradation steps all the complexes observed the major mass loss at 350- 600 °C. After thermal decomposition the residue remains as a metal oxide. In nitrogen atmosphere the substituted metal imino phthalocyanines complexes are very slow thermal decomposition. The 64% that was decomposed at 700 °C complex CoTTImPc, while for CuTTImPcmet with 58% mass loss , NiTTImPc with 55% and ZnTTImPc with 48% mass loss. In air the complexes are shows the higher stability like CoTTImPc > CuTTImPc > NiTTImPc > ZnTTImPc. Boride’s method was used to evaluate the kinetic and thermodynamic parameters. and all the degradation

Table 2: XRD and magnetic susceptibility measurements

Complex Name	2q angle (d Å)	(Relative Intensity) (%)	Field strength (KGauss)	Magnetic measurement $\chi_m \times 10^{-6}$ cgs units	μ_{eff} (B.M)
CoTTImPc	9.32 (10.32)	100	2.2	3265.87	2.73
	28.81 (4.07)	91.36	2.66	3035.41	2.55
	24.43 (2.43)	89.16	3.1	2838.16	2.41
			3.58	2713.64	2.34
			4.01	2540.26	2.19
CuTTImPc	6.80 (12.79)	100	2.2	3145.62	2.69
	8.58 (10.82)	92.27	2.66	3003.16	2.57
	29.92 (3.47)	90.45	3.1	2851.79	2.43
			3.58	2702.61	2.31
			4.01	2514.19	2.17
NiTTImPc	6.89 (14.72)	100	2.66		
	8.82 (10.17)	89.69		-747.51	---
	27.26 (3.47)	84.24			
ZnTTImPc	6.88 (14.57)	100	2.66		
	8.79 (11.18)	92.78		-1041.02	---
	25.94 (2.83)	94.15			

steps are exothermic in nature as per DTA results. The loss of periphery-tetra-1-(thiophene-2-yl) methanimine phthalocyanine complexes by the energy of activation (E_a) between the range of 0.87-4.79 KJ/mole. The breaking of the main phthalocyanine complex ring takes place with the immediate removal of periphery substituents. By the

negative entropies of the degradation, exothermic behavior of degradation was clearly indicated. Even there entropies are negative from -158.64 to -176.16 KJ. It was clearly indicated decomposition that the removal of functional groups. By using standard equations enthalpy, entropy and free energy was computed in Table 4.

Table 3: Thermodynamic degradation pattern

Complexes Name	Decomposition [°C]	Weight Loss (%)		
		Found	Calcd	Fragmentation
CoTTImPc	250-350	28.84	30.04	4-Imino groups
	350-600	65.46	65.83	Phthalocyanine moiety
CuTTImPc	250-350	28.82	30.15	4-Imino groups
	350-600	65.96	65.01	Phthalocyanine moiety
NiTTImPc	250-350	28.79	30.19	4-Imino groups
	350-600	65.87	65.19	Phthalocyanine moiety
ZnTTImPc	250-350	28.64	30.1	4-Imino groups
	350-600	65.52	65.11	Phthalocyanine moiety

Table 4: Kinetic and thermodynamic data in inert atmosphere and air

Complexes Name		E_a (kJ mole ⁻¹)	Frequency factor. (lnA min ⁻¹)	Enthalpy (kJmole ⁻¹)	Entropy (kJ mole ⁻¹)	Free energy (kJ mole ⁻¹)
CoTTImPc	I	4.79	5.2	-1.69	-164.03	62.45
		-0.75	-3.03	(-1.27)	(-160.10)	-61.56
	II	4.46	4.39	2.74	-152.07	81.59
		-1.51	-5.47	(-1.41)	(-149.67)	-79.52
CuTTImPc	I	0.87	6.34	-1.37	-176.16	74.86
		-0.68	-3.35	(-1.14)	(-174.11)	-74.69
	II	4.64	7.39	2.79	-143.82	79.42
		-1.25	-4.65	(-1.32)	(-141.89)	-77.24
NiTTImPc	I	1.43	5.2	-1.21	-158.64	72.79
		-0.71	-2.22	(-0.74)	(-157.49)	-70.48
	II	5.86	4.42	-0.85	-149.75	81.66
		-1.53	-4.82	(-0.83)	(-143.64)	-80.23
ZnTTImPc	I	1.92	3.36	-0.95	-175.84	75.42
		-0.63	-2.43	(-1.50)	(-173.41)	-74.75
	II	8.53	7.78	2.74	-142.51	82.48
		-5.57	-6.46	(-1.53)	(-140.67)	-80.92

(I & II indicated as degradation in nitrogen atmosphere)

CONCLUSION

Synthesis of substituted metal phthalocyanines was adopted by simple modified

method. The Copper and Cobalt phthalocyanine complexes are paramagnetic in behavior measured by magnetic susceptibility studies. The variation of magnetic moments with magnetic field

[2.20 to 4.01 KG] clearly indicated the presence of intermolecular co-operative effect in the compound. These complexes are poor in crystallinity in nature. The stability of the complexes in gravimetric analysis in an inert atmosphere like CuTTImPc > CoTTImPc > NiTTImPc > ZnTTImP.

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