

Synthesis and Studies on 2,9,16,23-tetra anilido nickel (II) Phthalocyanines.

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Abstract: A simple method has been developed for the synthesis of symmetrically substituted 2, 9, 16, 23-tetra anilido nickel (II) phthalocyanines via condensation of 2, 9, 16, 23-tetra carboxy nickel (II) phthalocyanine with aniline and 4-substituted anilines. These complexes are characterized using physico-chemical methods like elemental analysis, electronic, IR spectral, thermal and X-ray powder diffraction studies. Kinetic and thermodynamic parameters associated with the thermal decomposition of the synthesized complexes were calculated using thermo gravimetric analytical data.

Keywords: Tetra anilido nickel (II) phthalocyanines, thermal studies, Kinetic and thermodynamic parameters.

INTRODUCTION

Metal phthalocyanine complexes have world-wide interest in the field of dyes and pigments since their discovery in the year 1907 [1, 2], because of their outstanding stability to light, heat, acids and alkalis [3]. Structural similarities of these compounds with naturally occurring biologically important molecules like chlorophyll and hemoglobin, forced the researchers to study the physico-chemical properties of phthalocyanines [4]. Various substituted metal phthalocyanines have also been reported as conductors, semiconductors [5], photoconductors, photovoltaic materials, liquid crystals, catalysts, Photodynamic therapy (PDT) of tumors, corrosion inhibitors, solar cell functioning materials, gas sensors, nonlinear optical limiting devices etc[6-10]. Many reports are available on the synthesis and structural investigations of 2, 9, 16, 23 and 1, 8, 15, 22-

symmetrically tetra substituted metal phthalocyanines [11-13]. However no reports are available on the synthesis and characterization of 2, 9, 16, 23-tetra anilido substituted nickel (II) phthalocyanines. Keeping the above facts in mind, we have undertaken the synthesis and characterization studies on the title complexes. In the present paper we have discussed synthesis and characterization of 2, 9, 16, 23-tetra anilido substituted nickel (II) phthalocyanine and its para-substituted derivatives. Thermal studies were carried in order to exploit the thermal stability of the complexes

All the newly synthesized 2, 9, 16, 23- tetra anilido substituted nickel (II) phthalocyanines are dark green in color. Characterization of these complexes was difficult because of their insolubility in almost all organic solvents. Nevertheless, the elemental analysis, IR, UV-Vis, powder X-ray diffraction (XRD), and

thermal analyses provided sufficient evidences for the proposed structures.

EXPERIMENTAL

MATERIALS AND METHODS;

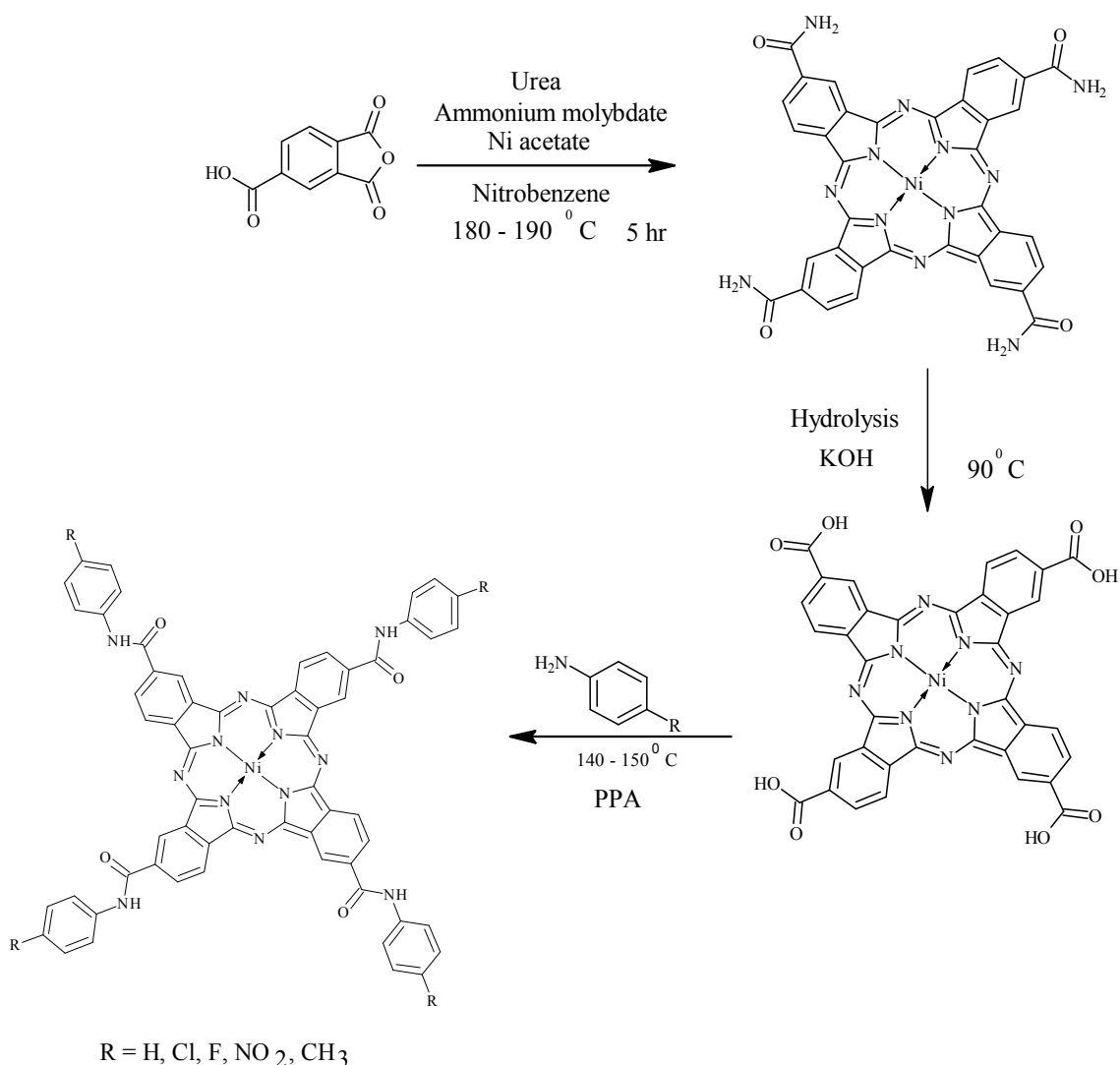
1, 2, 4-Benzene tricarboxylic anhydride was purchased from Aldrich and other chemicals were obtained from Merck (India) and used as such for the synthesis. Tetracarboxy nickel phthalocyanine is prepared according to the reported procedure with slight modification [14]. IR spectra of the complexes were recorded in KBr pellets on Nicolet MX-1FT-IR spectrometer in the wavelength range of $4000\text{--}400\text{cm}^{-1}$. Thermal analysis was carried out in SHIMADZU TA-60WS Thermal Analyzer in air at a heating rate of 5°C min^{-1} .

SYNTHESIS OF TETRACARBOXY NICKEL (II) PHTHALOCYANINE

The general route for the synthesis of title complexes is given in **scheme 1**. Nickel (II) tetra formamido phthalocyanine was prepared by the reaction of 1, 2, 4-

benzene tricarboxylic anhydride (50g; 1mole), nickel acetate (26g; 0.4mole), ammonium chloride (10g; 0.45 moles), catalytic amount of ammonium molybdate and excess of urea (~100g) in 100 ml of nitrobenzene in three necked flask for 5 hours at 185°C . A blue-green solid nickel (II) tetra formamido Pc formed was transferred into 2M potassium hydroxide solution and the reaction was carried out at 90°C for 10 hrs until no ammonia was evolved. The resulting solution was diluted with required amount of water and was brought to $\text{pH} < 3$ with concentrated hydrochloric acid and then filtered. The residue was redissolved with 0.5 M potassium hydroxide solution and filtered. The resulting solid was washed with water several times and then with methanol until a solid with metallic luster of tetra carboxylic Nickel (II) Phthalocyanine was obtained. Finally it was dried over anhydrous P_2O_5 .

SCHEME 1: SYNTHESIS OF TETRA ANILIDO NICKEL (II) PHTHALOCYANINE AND ITS DERIVATIVES.



SYNTHESIS OF TETRA ANILIDO NICKEL (II) PHTHALOCYANINE AND ITS DERIVATIVES

4 equivalents of aromatic primary amine (aniline) and 1 equivalent of an acid (tetra carboxy nickel (II) phthalocyanine) was taken in a 100g of pre heated polyphosphoric acid (PPA) in a 250 mL round bottomed flask equipped with a condenser and

mechanical stirrer. The reaction was carried out at 140-150°C for 15 hours. The reaction mixture was poured in to ice cold water. The precipitate obtained was filtered, washed thoroughly with water and then treated with 1N sodium hydroxide till free from polyphosphoric acid. Further, the product obtained was treated with alcohol and dried over anhydrous P_2O_5 .

TABLE-1: THERMODYNAMIC AND KINETIC PARAMETERS.

Complex compound	Decomposition Range($^{\circ}C$)	E_a (kJ mol $^{-1}$)	$\ln A$ (s $^{-1}$)	ΔH (kJ mol $^{-1}$)	ΔS (kJ mol $^{-1}$)	ΔG (kJ mol $^{-1}$)
TcNi(II)Pc	350-400	187.6	10.02	-1.4826	-146.3	95.04
	460-480	28.14	8.127	-1.4521	-146.2	107.3
TANi(II)Pc	470-500	102.2	9.416	-1.0144	-142.4	109.5
TCNi(II)Pc	370-480	5.499	6.494	-1.4517	-146.6	103.8
TFNi(II)Pc	480-518	17.40	7.646	-1.4192	-145.4	115.0
TNNi(II)Pc	470-506	11.80	7.258	-1.3825	-145.4	112.7
TMNi(II)Pc	420-512	13.08	7.361	-1.417	-145.8	110.0

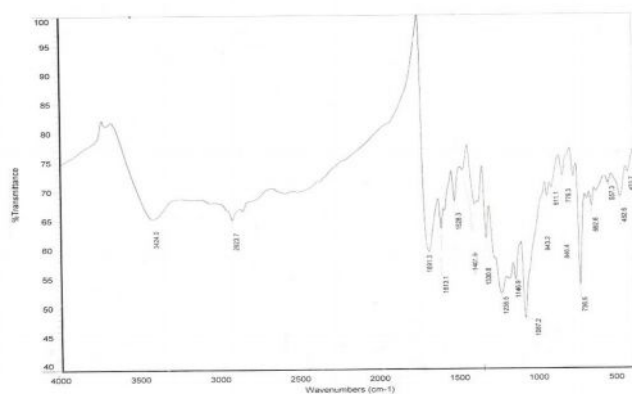


Fig.1a. [TcNi(II)Pc]

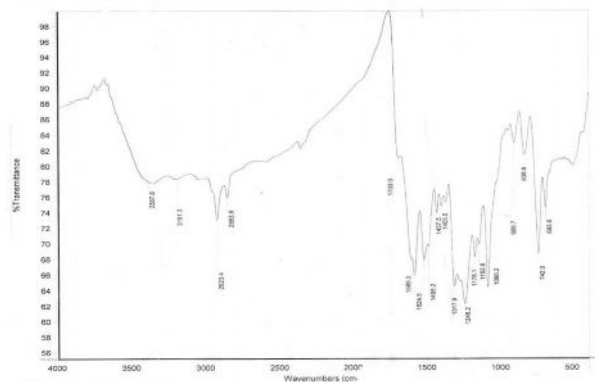


Fig.1b. [TANi(II)Pc]

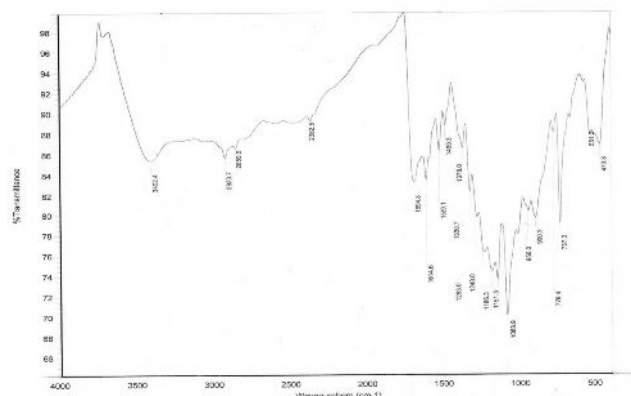


Fig.1c. [TCNi(II)Pc]

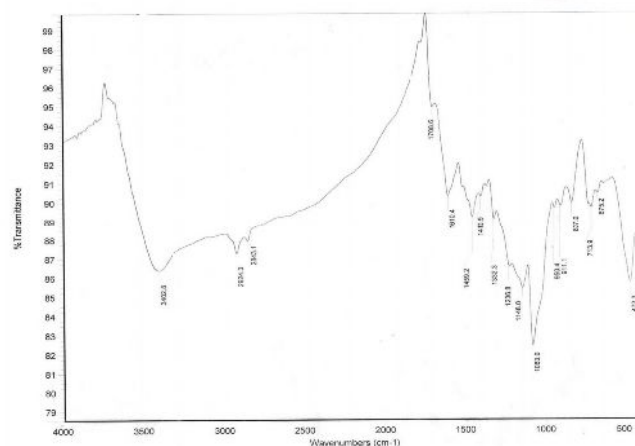


Fig.1d. [TcNi(II)Pc]

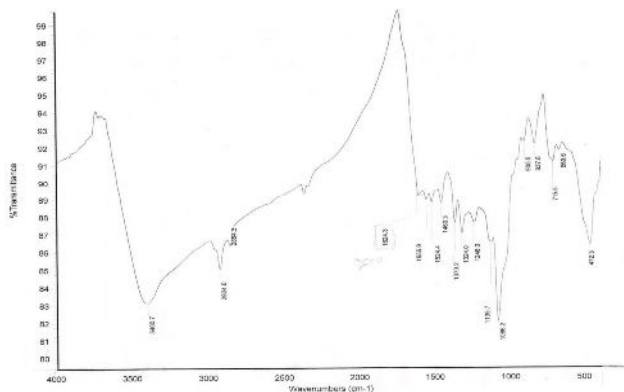


Fig.1e.[TN Ni(II)Pc]

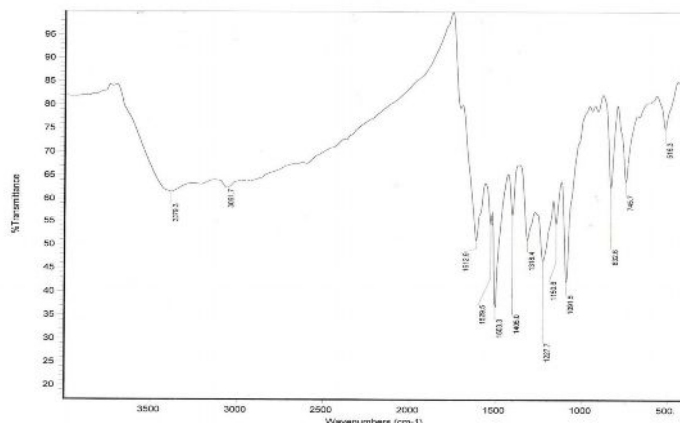


Fig.1f.[TMNi(II)Pc]

RESULTS AND DISCUSSION

The metals with atomic radii very close to $1.35 \text{ \AA}$ forms metal phthalocyanine complexes which makes them thermally stable and resistance towards concentrated sulfuric acid. Tetra anilido substituted nickel Phthalocyanine and its para-substituted derivatives are synthesized with a very good quantitative yield. These phthalocyanines have dark greenish to black in color. The elemental analysis for carbon, hydrogen, oxygen and nitrogen are agreed very well with the theoretical calculations indicating the good purity of the synthesized compounds. The tetra anilido nickel (II) Phthalocyanines are relatively poor crystalline than the corresponding tetra carboxy nickel (II) Phthalocyanine. The proposed structures of the synthesized complexes are as shown in Schemel.

IR spectra of the synthesized complexes are recorded in the region $400\text{--}4000 \text{ cm}^{-1}$ using the KBr and are given in **Fig 1a-1f**. Various IR signals responsible for different vibrations of the functional group cannot be identified separately, since most of the stretching vibrations lie in the complicated region of the skeletal vibrations of the phthalocyanine molecule. However, the presence of functional groups in the periphery is confirmed by their characteristic bands.

Tetra carboxy nickel (II) phthalocyanine [TcNi(II)Pc] : Elemental analysis; (Calculated%) Found%; C(57.86)57.66, H(2.16)2.26, N(15.00)15.05 Ni(7.85)7.76 O(17.13)17.27; 3424 cm^{-1} ($-\text{OH}$ group of $-\text{COOH}$), 1528 cm^{-1} (Ar. C=N stretching), sharp signal at 1691 cm^{-1} (C=O) and $2923, 1613, 1613 \text{ cm}^{-1}$ reflects on the skeletal vibrations of the phthalocyanine molecule.

Tetra anilido nickel(II) phthalocyanine [TANi(II)Pc] : C(68.78)68.01, H(3.46)3.66, N(16.04)16.77, Ni(5.60)5.46, O(6.11)6.77; 1703 cm^{-1} (C=O), 3191 cm^{-1} (NH), 2923 cm^{-1} (Ar. C=N), 1524 cm^{-1} (Ar. C=H).

Tetra chloro anilido nickel(II) phthalocyanine [TCANi(II)Pc] : C(60.79)60.69, H(2.72)2.82, Cl(11.96)11.81, N(14.18)14.23, Ni(4.95)4.93, O(5.40)5.52; 1694 cm^{-1} (C=O), 3402 cm^{-1} (NH), 2923 cm^{-1} (Ar. C=H), 1529 cm^{-1} (Ar. C=N) and 737 cm^{-1} (C-Cl).

Tetra fluoro anilido nickel(II) phthalocyanine [TFANi(II)Pc] : C(64.36)64.26, H(2.88)2.95, F(6.79)6.76, N(15.01)15.08, Ni(5.24)5.19, O(5.72)5.79; 1708 cm^{-1} (C=O), 3402 cm^{-1} (NH), 2924 cm^{-1} (ar CH), 1459 cm^{-1} (ar C=N), 1089 cm^{-1} (C-F).

Tetra nitro anilido nickel(II) phthalocyanine [TNANi(II)Pc]; C(69.64)69.44, H(4.02)4.20, N(15.23)15.15, Ni(5.32)5.40, O(5.80)5.87; 1624 cm^{-1} (For C=O), 3400 cm^{-1} (NH), 2924 cm^{-1} (ar CH), (ar C=N) 1524 cm^{-1} .

Tetra methyl anilido nickel(II) phthalocyanine [TMANi(II)Pc]; C(58.70)58.11, H(2.63)2.82, N(18.25)18.38, Ni(4.78)4.98, O(15.64)15.69; 1612 cm^{-1} (C=O), 3379 cm^{-1} (-NH), 3061 cm^{-1} (Ar.CH), 1529 cm^{-1} (ar. C=N).

A UV- Visible Spectrophotometer UV-160 A from SHIMADZU CORPORATION JAPAN with 1 cm matched cells was used for the electronic spectral measurements. Electronic spectra of tetra carboxy nickel (II) phthalocyanine, tetra-anilido nickel (II) phthalocyanine has been recorded in dimethyl sulphoxide (DMSO) for the sake of comparison and is given in Fig.3. The electronic spectra of the complexes

under investigation exhibited two major absorption bands. An intense Q band appeared in the wavelength range 500-700 nm with the log ϵ values ranging from 1.6 to 2.2×10^4 , and a comparatively wider B band at 300-400 nm. The Q band of tetra carboxy nickel(II) phthalocyanine appeared in the range of 600-605nm; the Q band of the tetra anilido nickel(II)

phthalocyanine exhibited red shift of 74-79 nm with respect to the corresponding tetra carboxy nickel phthalocyanine. This can be attributed for the fact that the peripheral substitution of anilido linkage enhanced the extended delocalization of π electrons of phthalocyanine molecules.

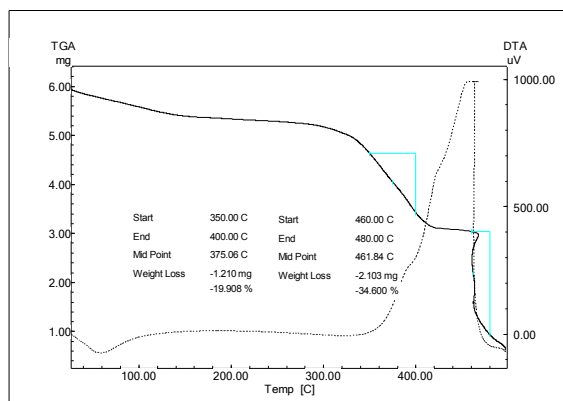


Fig.2a[TcNi(II)Pc]

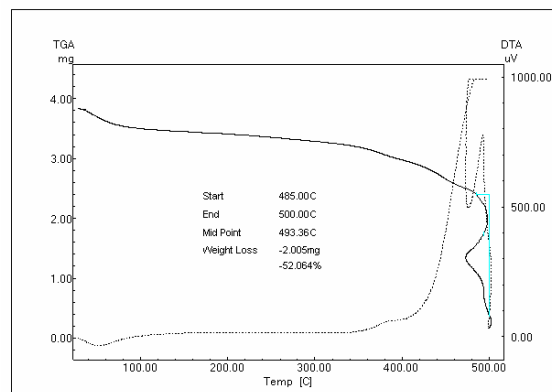


Fig.2a[TANi(II)Pc]

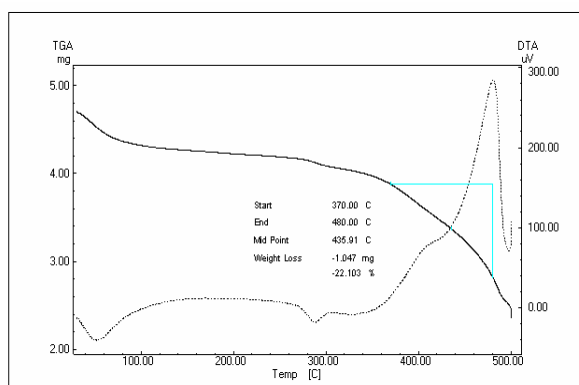


Fig.2c.[TCNi(II)Pc]

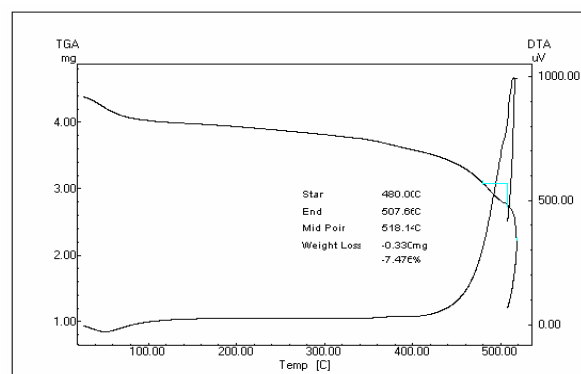


Fig.2d.[TFNi(II)Pc]

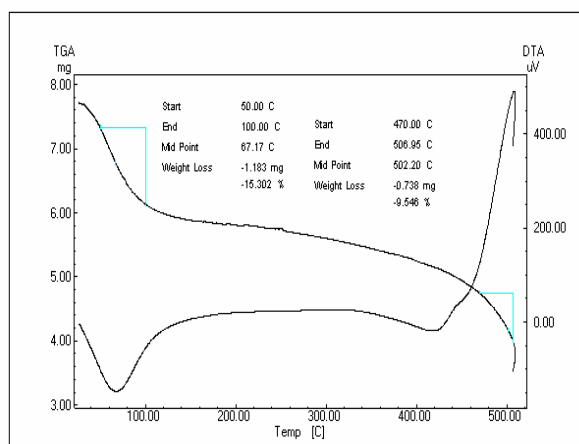


Fig.2e. [TN Ni(II)Pc]

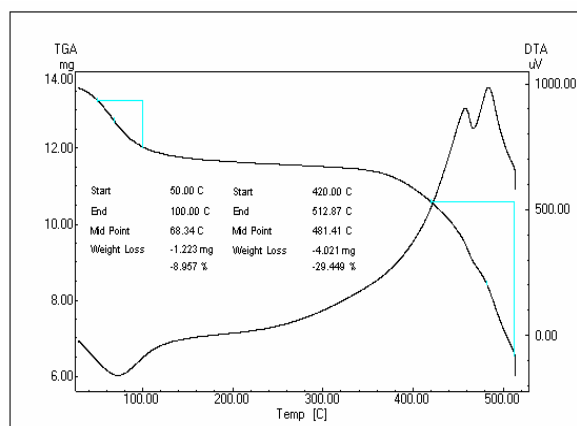


Fig.2f.[TMNi(II)Pc]

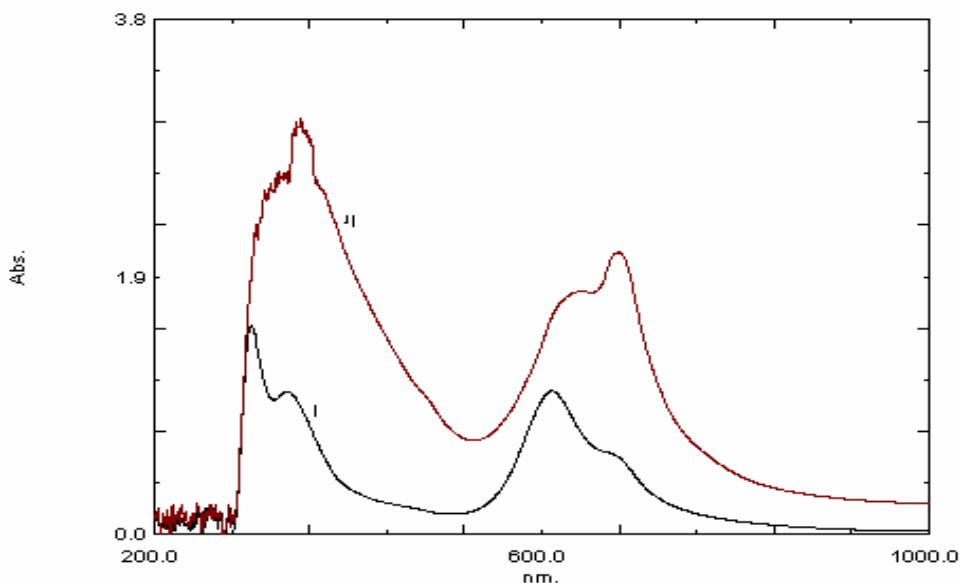


Fig.3; Uv-visible spectra of (1)TcNi(II)Pc and (2)TANI(II)Pc

THERMO GRAVIMETRIC STUDIES

Thermal analysis of the synthesizing complexes was carried out in SHIMADZU TA- 60WS thermal analyzer in air at a heating rate of $5^{\circ}\text{C min}^{-1}$ and the TGA and DTA curves are given in the Figs. 2a-2f. TG analytical curve obtained for title complexes showed that the decomposition of tetra carboxy nickel phthalocyanine [TcNi(II)Pc] occurs in two steps. The first step of degradation occurs in a temperature range $350 - 400^{\circ}\text{C}$ and the second step of decomposition occurs in the temperature range of $460 - 480^{\circ}\text{C}$. The tetra anilido nickel phthalocyanine and its para substituted derivatives exhibited the gradual decomposition in one step. TANI(II)Pc ($470-500^{\circ}\text{C}$) TCANI(II)Pc ($370-480^{\circ}\text{C}$), TFANI(II)Pc ($480-518^{\circ}\text{C}$), TNANI(II)Pc ($470-506^{\circ}\text{C}$), TMANi(II)Pc ($420 - 512^{\circ}\text{C}$). Hence tetra anilido nickel Phthalocyanine and its derivatives are comparatively thermally more stable than tetra carboxy nickel phthalocyanine. DTA results revealed that all degradation steps are exothermic in nature. Kinetic and thermodynamic parameters of the complexes have been evaluated by Broido's method [15-16]. Plots of $\ln(-\ln 1/y)$ versus $1/T$ (where Y is the fraction of the complex undecomposed) were developed and from that the energy of activation (E_a) and frequency factor ($\ln A$) were evaluated. Enthalpy (ΔH), Entropy (ΔS) and free energy (ΔG) have been computed using standard equations. The data are summarized in the table 1.

$$\Delta H = E_a - RT \quad (1)$$

$$\Delta S = \Delta H/T - 19.15 \log T / \text{K} - 197.57 \quad (2)$$

$$\Delta G = \Delta H - T \Delta S \quad (3)$$

$$A = RT / Nh e^{\Delta S/R} \quad (4)$$

Where R = gas constant, T = degradation temperature in K, k = rate constant, N = Avogadro's number, h = Plank's constant.

X-RAY DIFFRACTION STUDIES

The powder X-ray diffraction pattern of tetra-anilido nickel (II) phthalocyanines are obtained using Cu- $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). X-ray diffraction studies for the complexes are done in the range 2θ angles $2-70^{\circ}$. The X-ray diffraction pattern of the complexes showed many sharp peaks in the spectrum indicating the crystalline nature of the sample. The non crystalline portion simply scatters the X-ray beam to give a continuous base line or background. The 2θ angles are obtained from the patterns of the samples, intra planar spacings (d) are calculated using the Bragg's equation, $2d \sin \theta = n\lambda$, where θ = angle of diffraction, n = an integer called as order of interference and λ = wavelength of radiation. Crystallinity of the samples were calculated by using Scherer's formula $D(hkl) = K\lambda / \beta \cos \theta$, where D is the average crystal size, λ is the wavelength of the X-ray irradiation, β is the full width half maxima(FWHM) of

diffraction peak corrected for the instrumental line broadening using silicon as a standard, and θ is angle of diffraction. It was found that the tetra anilido nickel

REFERENCES

- [1] Braun .A, Tcherniac .J, Ber. 1907 , 40, 2709.
- [2] (a) Moser F.H, Thomas A.L, The Phthalocyanines, , CRC Press, Boca Raton, 1&2, 1983;
- b) Libbert. G, Ullmann's Encyclopedia of Organic Compounds, A 20,1992, 213.
- [3]Gregory P. Industrial applications of phthalocyanines 2000; 4,432.
- [4]Kato.M, Nishioka.Y, Kaifu.K, Kawamura. K., Ohno. S, Appl.Phys. Lett. 1985, 46, 196.
- [5] Harish. M.N.K, Keshavayya.J, Venugopala reddy. K.R,. Mallikarjuna.H.R,. Shoukat ali.R.A and Rajesh.T, J. co-ord.Chem - 2010,63, 4050
- [6] Chen.H, Wang.W and Feng.L, J. Polym. Sci. Part A, 1995, 1165.
- [7]Loutfy. R.O, Sharp .J.H.J. Chem. Phys. 1979,71,1211.
- [8] Wohrle.D, Meissner.D, Adv. Mater. 1991, 03,129.
- (II) phthalocyanine and its derivatives (14-24nm) are relatively poor crystalline than the tetra carboxy nickel (II) phthalocyanine (33.4nm).
- [9] Beatriz Cabezo'n, Monica Nicolau, Joaquín Barbera , and Toma's Torres. Chem. Mater; 2000, 12,776.
- [10]Vishal B. Sharma, Suman L. Jain and Bir Sain . 2004, 98,141.
- [11]Donata Dei J. Porphyrins and Phthalocyanines; 2006, 10,147.
- [12]Somashekarappa.M.P, Venugopala Reddy.K.R, Harish.M.N.K, and Keshavayya.J – J. Mol. Struct; 2005, 753,190.
- [13]Venugopala Reddy.K.R, Harish.M.N.K and Keshavayya. J , J. Fluorine Chem.; 2007,128,1019.
- [14]Achar,George M.Fohlen, and John A Parker; united state patent; 1984. 4,450,268,
- [15]Laidler .K.J, Chemical Kinetics, Tata McGraw-Hill; 2nd Ed, 1972.
- [16]Daniels. F, Alberty R.A, Physical Chemistry, John Wiley, New York, 1995.
