

Synthesis and characterization of lead phthalocyanine and its derivatives

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Abstract

Lead (II) phthalocyanine (PbPc); lead (II) tetranitro phthalocyanine (PbTNP) and lead (II) tetraamino phthalocyanine (PbTAP) are synthesized in pure state. These complexes are characterized using elemental analysis, UV–visible, IR-spectroscopy, X-ray crystallography and thermogravimetry. Kinetic and thermodynamic parameters associated with the thermal decomposition were calculated using thermogravimetric data. Electrical conductivity studies are done for all the three complexes using two-probe technique in the temperature range from 30 to 200 °C. The electrical conductivity observed at 30 °C are in the order PbTAP > PbTNP > PbPc. The relevant electrical conductivity data observed are reported.

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1. Introduction

Metal phthalocyanines are the important class of organic materials, which have attracted the world-wide interest because of their properties like very high thermal stability, chemical inertness, high colouring property, semiconductivity, photoconductivity, catalytic activity, etc. [1–7]. These materials find interesting applications in photocells [8,9], nonlinear optics [10], gas sensors [11,12], in the treatment of cancerous tissues [13,14] and the like. The phthalocyanine ring is having planar structure which forms a number of derivatives by replacing the central two hydrogen atoms by a variety of divalent, trivalent, tetravalent metals and metalloids. Electrical conductivity is one of the properties which has received considerable attention since 1948 [15,16]. The conducting properties of these materials are sensitive to the nature of the central metal or metalloid, substituents at the peripheral benzene rings and the surrounding atmosphere. The electrical conductivity

changes by many orders of magnitude under the influence of gases [17] and in presence of dopants [18,19].

Lead phthalocyanine is of special interest because of its nonplanar “shuttle-cock” structure with C_{4v} molecular symmetry [20] and the lead phthalocyanine film’s electrical conductivity sensitivity to NO_2 [21].

Lead phthalocyanine has been synthesized by solid state [22] and solution [23] methods. However, the condition for the synthesis of lead phthalocyanine by solid state method found to give no lead phthalocyanine and the solution method proposed earlier give very low yield (16%). Lead tetranitro and lead tetraamino phthalocyanines are not been synthesized so far. But mention has been made of amino substituted and nitro substituted phthalocyanines in a Japan patent [24]. The synthetic procedure and the nature of nitro and amino substituted phthalocyanine are not clear. The present research work deals with the synthesis of lead phthalocyanine, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine in pure state with very high yield (85–90%). These materials are characterized using elemental analysis, UV–visible and powder X-ray diffraction studies. Electrical conductivity studies have been carried out for the above three synthesized materials over the temperature range 30–200 °C and the results are presented here.

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2. Materials and methods

2.1. Synthetic procedures

2.1.1. Synthesis of lead (II) phthalocyanine (PbPc)

Lead phthalocyanine was synthesized by modifying the procedure described by Linstead and co-workers [22]. A brief summary of the procedure is given here.

A 10 g (0.078 mol) phthalonitrile was heated to 180 °C until it completely melts. Then 5 g (0.022 mol) lead monoxide was added in small portions to the completely molten solution. The reaction mixture was maintained at 180 °C for 90 min with constant stirring. The solid product was finely ground and washed with glacial acetic acid and hot alcohol. The dark green product obtained was dried in oven at 70 °C for 2 h.

Anal. Calc. for lead (II) phthalocyanine, $C_{32}H_{16}N_8Pb$: C, 53.39; H, 2.22; N, 15.57. Found: C, 53.21; H, 2.24; N, 15.45%. UV–visible electronic absorption bands, λ_{max} (nm): 334, 443, 635, 705 (DMSO). IR absorption bands (cm^{-1}): 3052m, 1607w, 1478s, 1401m, 1330s, 1282m, 1160m, 1114s, 1079s, 1059s, 1005m, 953m, 879s, 815m, 772s, 723s, 625m, 565w, 496m.

2.1.2. Synthesis of lead (II) tetranitro phthalocyanine (PbTNP)

Lead tetranitro phthalocyanine was synthesized by heating 13.5 g (0.078 mol) 4-nitrophthalonitrile to 160 °C until it melts completely. Then 5 g (0.02 mol) of lead monoxide was added in small portions with constant stirring. The reaction mixture was maintained at 140 °C with constant stirring for 4 h. The deep green solid was obtained by purifying using the procedure as explained for PbPc.

Anal. Calc. for lead (II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Pb$: C, 42.70; H, 1.33; N, 18.68. Found: C, 42.77; H, 1.38; N, 18.75%. UV–visible electronic absorption bands, λ_{max} (nm): 302, 654, 715 (DMSO). IR absorption bands (cm^{-1}): 3095m, 1610m, 1521s, 1483m, 1337s, 1252m, 1135s, 1081s, 921m, 846s, 749s, 728s, 671m, 477s, 435s.

2.1.3. Synthesis of lead (II) tetraamino phthalocyanine (PbTAP)

Lead tetraamino phthalocyanine was prepared by the reduction of nitro derivative using sodium sulphide [25]. An outline of the procedure is given below.

A 4 g of PbTNP was placed in 100 ml water. To this slurry 20 g of sodium sulphide nonahydrate was added and stirred at 50 °C for 5 h. The solid product was separated and washed with 0.5 M hydrochloric acid and 1 M sodium hydroxide solution. Finally, the compound was washed with water until the filtrate is neutral to litmus paper. The dark blue coloured product was dried in oven at 50 °C.

Anal. Calc. for lead (II) tetraamino phthalocyanine, $C_{32}H_{20}N_{12}Pb$: C, 49.28; H, 2.56; N, 21.56. Found: C,

49.32; H, 2.53; N, 21.61%. UV–visible electronic absorption, λ_{max} (nm): 337, 735 (DMSO). IR absorption bands (cm^{-1}): 3356w, 3224w, 3056w, 2741m, 1714s, 1611s, 1497s, 1328s, 1120m, 1099m, 1033w, 967m, 867w, 833m, 746s, 527w, 421s.

2.2. Elemental analysis and physical measurements

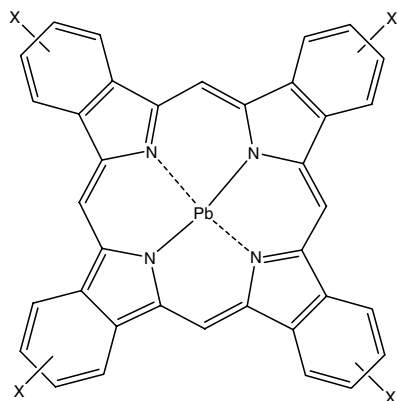
Elemental analysis for carbon, hydrogen and nitrogen were done using Vario EL III CHNS analyzer, Germany. UV–visible spectra were recorded in DMSO using Systronics-117 spectrophotometer with 1.0 cm quartz cells, Systronics, Ahmedabad, India. IR spectra were recorded using JASCO FT/IR-460 Plus spectrophotometer, Japan. A Rigaku Miniflex X-ray diffractometer, model IGC-2, Rigaku Denki Co. Ltd., Japan. Source: $Cu\ 1.54060\ \lambda$ was used to study the powder X-ray diffraction of the samples. All the samples were compressed into pellets of 1.30 cm diameter and thickness ranging around 0.2 cm using Perkin–Elmer KBr Die under a pressure of 500 kg/cm². The carver laboratory press model – diaton capacity was been used for applying the pressure. Conducting silver paint was coated on both flat surfaces of the pellets and the electrical contact with electrode is made using the same silver paint. The resistance measurements were done using DOT-402 Digital Milli Ohm meter and DOT-425 Insulation Resistance Tester, Bhandari Electronics and Electricals, Bangalore, India. Thermogravimetric analysis were performed in air atmosphere using TGA-7 Analyzer, Perkin–Elmer, USA from ambient temperature to 700 °C at a heating rate of 10 °C/min and with a flow rate of air at 30 ml/min.

3. Results and discussion

Lead phthalocyanine has been synthesized in pure state by adapting the procedure proposed by Barrett et. al. [22] with very high yield 85%. Simple and commercially important procedures are developed to synthesize lead tetranitro and lead tetraamino phthalocyanines (Fig. 1). The synthetic procedures gave very high yield. The elemental analysis for carbon, hydrogen and nitrogen agreed well with the theoretical values indicating the very high purity of the complexes. The IR and UV–visible spectral data of PbPc are in good agreement with the earlier reported values [26–28].

3.1. Electronic spectra

PbPc, PbTNP and PbTAP are soluble in concentrated sulphuric acid (>28 N H_2SO_4) and dimethyl sulphoxide. But these complexes are not stable in sulphuric acid medium [29] and hence electronic spectra are recorded in dimethyl sulphoxide solvent in the range 260–800 nm (Fig. 2). The UV cut-off region for DMSO is 265 nm. All the synthesized lead phthalocyanine complexes are stable



X

H : Lead phthalocyanine

NO₂ : Lead tetranitro phthalocyanine

NH₂ : Lead tetraamino phthalocyanine

Fig. 1. Structure of lead phthalocyanine derivatives.

in DMSO medium for more than a week. The peaks obtained in the Q-band region in the range 735–635 nm are responsible for the observed green colour of the complexes. These transitions may be assigned to the $\pi \rightarrow \pi^*$ transitions [30]. The peaks obtained in the B-band region are in the range 302–337 nm. The broad absorption peaks observed at 443 and 465 nm for PbPc and PbTNP, respectively may be due to C_{4v} symmetry of the complexes [27]. Substitution of the electron donor –NH₂ group on the peripheral benzene ring of the PbPc structure found to effect hypsochromic shift to an extent of 32 nm. The substitution of the electron acceptor –NO₂ group found to affect bathochromic shift to a very small extent of 3 nm in comparison to the peak observed in the spectrum of PbPc complex. The UV–visible electronic spectral studies in sulphuric acid medium are reported elsewhere [26,30].

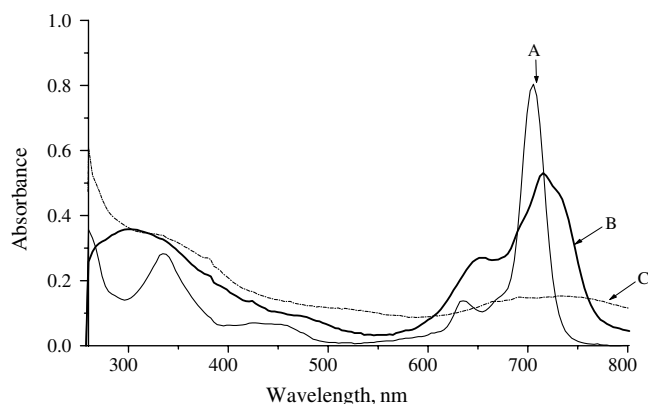


Fig. 2. Electronic spectra of PbPc (A), PbTNP (B) and PbTAP (C) in DMSO.

3.2. IR spectral study

IR spectra of PbPc, PbTNP and PbTAP are recorded in the fundamental region of 400–4000 cm⁻¹, using KBr disc technique. The IR spectra recorded for the three complexes are presented in Fig. 3. All the complexes showed absorption peaks around 723–746, 833–879, 921–967, 1028–1059, 1079–1099 and 1114–1135 cm⁻¹ which may be assigned to phthalocyanine skeletal vibrations [31]. The absorption bands at 1521 and 1337 cm⁻¹ are observed in the IR spectrum of PbTNP complex, which may be assigned to the asymmetric (ν_{as}) and symmetric (ν_s) stretching due to the nitro groups present in the structure of the complex. Two weak absorption bands are observed at 3356 and 3224 cm⁻¹ in the IR spectrum of PbTAP complex due to the asymmetric and symmetric stretching of the amino group. All the spectra showed absorption peaks in the range 3052–3095 cm⁻¹ assignable to the aromatic C–H stretching as well as absorption bands around 1478–1497 cm⁻¹ assignable to c–c bond.

3.3. Powder X-ray diffraction

The 2θ values observed for all the three complexes are used in the analysis for the possible crystal structures of the compounds using the procedure DICVOL 91 as outlined elsewhere [32,33]. The lattice constants obtained and the probable crystal structures as observed by the analysis are summarised in Table 2. The analysed data indicate that all the complexes are having monoclinic structure.

3.4. Thermogravimetry

Thermogravimetric analytical studies done in the dynamic atmosphere of air indicated that the organic portions of the structures of all the three complexes (70–75%) found to degrade in one step above 400 °C. The decomposition temperatures DT (DT_{max} = maximum decomposition temperatures) observed are 400 °C (430 °C), 406 °C (422 °C) and 475 °C (550 °C) for PbPc, PbTNP and PbTAP respectively. The residual weights observed in the thermogravimetric analytical curves corresponded to lead oxide which agreed very well with the theoretical calculations. The thermal stabilities of these complexes are found to be in the order PbTAP > PbTNP > PbPc. The greater thermal stabilities observed for the substituted PbPc complexes may be explained due to the nature of electron donor amino group as in the case of PbTAP and electron acceptor nitro group as in the case of PbTNP. The substituted groups in the fragmented phthalonitrile of the phthalocyanine structure are expected to stabilize due to the contribution of various resonance structures. The greater thermal stability of PbTAP may be due to the greater contribution to the resonance stability of the fragmented structures by the electron donor amino group.

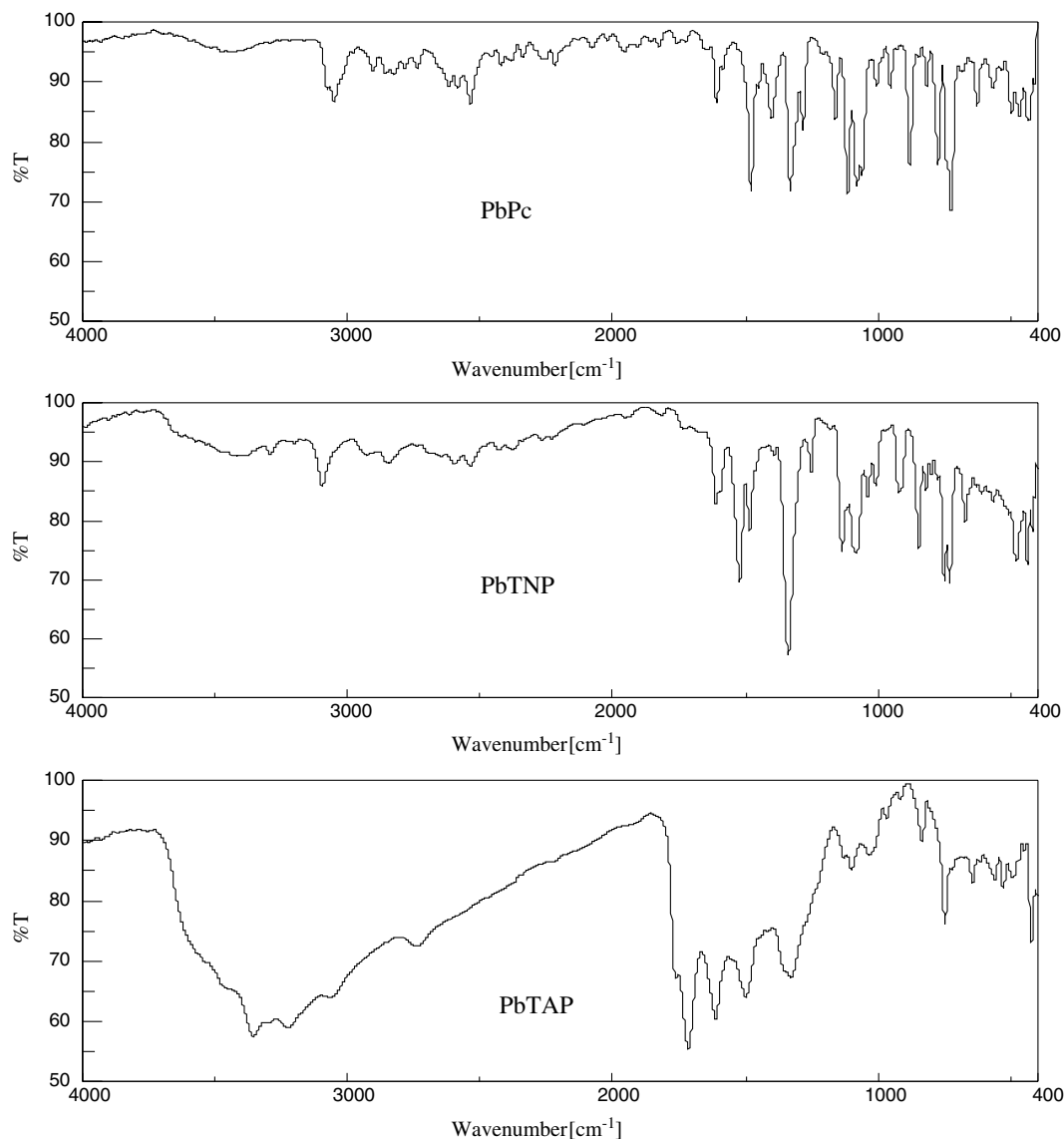


Fig. 3. IR-spectra of lead phthalocyanine, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine.

Broido's [34] graphical procedure is used for the region of first-order decomposition portion of the thermogravimetric analytical curves to evaluate activation energy. The graphical plots of $\ln [1n(1/y)]$ vs. $10^3/T$ obtained for PbPc, PbTNP and PbTAP are presented in Fig. 4. The value of 'y' represents the fraction of the compound remaining at the temperature T °C.

The plots indicate that all the three complexes degrade through a first-order process. The slopes of the plots are determined and used to evaluate the activation energies for the complexes and the data are presented in the Table 1. The activation energies observed are in the order PbTNP > PbPc > PbTAP. The activation energy depends on the chemical structure and the crystalline nature of the material. Greater the crystalline nature, greater will be the activation energy. The crystalline nature of the materials are also found to be in the same order of activation energies, as seen by the X-ray diffraction pattern [35].

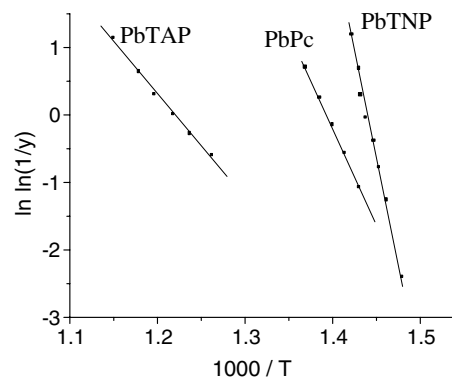


Fig. 4. First-order thermal degradation plots for lead phthalocyanine, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine.

The thermodynamic properties like change in enthalpy (ΔH), entropy (ΔS), free energy (ΔG) and frequency factor (A) are calculated using the standard equations as

Table 1

Thermodynamic and kinetic parameters for the thermal degradation process of lead phthalocyanine, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine

Compound	E_a (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	ΔG (kJ mol ⁻¹)	A (s ⁻¹)
PbPc	241.48	235.53	30.63	213.66	5.93×10^{14}
PbTNP	517.31	511.56	451.63	119.03	5.63×10^{36}
PbTAP	133.92	127.09	-145.08	246.20	4.52×10^5

explained elsewhere [36,37] and the values are summarised in Table 1. The first-order rate constant is determined based on the weight change with time in the linear degradation portion of the thermogravimetric curve and used for the evaluation of entropy change. The rate of degradation are in the order PbTNP > PbPc > PbTAP and the mechanism of degradation is seem to be same.

3.5. Electrical conductivity

At 30 °C the electrical conductivities observed for PbPc, PbTNP and PbTAP are 3.2×10^{-10} , 5.2×10^{-9} and 1.1×10^{-6} S cm⁻¹, respectively. The substitution of electron withdrawing -NO₂ groups found to increase 10 times the electrical conducting property of PbPc. Whereas the electron donor -NH₂ groups found to increase the electrical conductivity by 10⁴ times in comparison to the parent lead phthalocyanine. The variations of electrical conductivity over a temperature range 30–200 °C are studied for the three complexes and the electrical conduc-

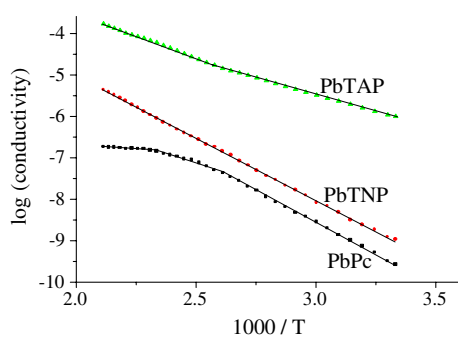


Fig. 5. Variations of electrical conductivities of lead phthalocyanine, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine.

tivity data are plotted $\log \sigma Vs 10^3/T$ (Fig. 5). The plots indicated that the electrical conductivity of PbPc is linear over the temperature range 30–95 °C, PbTNP showed linear electrical conductivity variation from 30–200 °C and PbTAP showed linear electrical conductivity variation in the temperature ranges from 30 to 125 °C and from 125 to 200 °C. The thermally activated varying electrical conductivity with temperature was found to obey the expression $\sigma = \sigma_0 e^{-E_a/KT}$ where, E_a is the activation energy, σ is the specific conductivity, σ_0 is a constant, K is Boltzmann constant and T is the absolute temperature. The relevant data are presented in Table 2. The variations of electrical conductivities of lead phthalocyanine complexes can be expected here due to the nature of the substituent group at the peripheral benzene group of phthalocyanine, overlap of the π electron system and the differences in the stacking of phthalocyanine molecules.

The powder X-ray diffraction study indicated that the cell parameters observed for PbPc, PbTNP and PbTAP complexes are 13.295, 10.096 and 8.213 Å which are in decreasing order. The electrical conductivity are found to be in increasing order. Though all the three complexes are found to have monoclinic structures, their cell parameters are found to be different (Table 2). These differences can be accounted for the differences in the electrical conductivities observed for the above three complexes. The 10⁴ times improvement in the electrical conductivity observed for PbTNP may be accounted for the stacking arrangement of the molecules with improved overlap of the π electron systems. Generally, decreasing the electron density of the phthalocyanine ring facilitates greater intermolecular contact because of the decreased repulsion between phthalocyanine rings. But electrical conductivity has been found to increase with the substitution of electron

Table 2

X-ray diffraction data and electrical conductivity data of lead phthalocyanine, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine

Compound	X-ray diffraction data			Electrical conductivity data		E_a (eV) (temperature range)
	Interplanar spacings (Å)	β	Volume	σ S cm ⁻¹ 30 °C	200 °C	
PbPc	$a = 13.295$ $b = 8.069$ $c = 9.092$	91.095	975.35	3.2×10^{-10}	1.8×10^{-7}	0.268 (30–95 °C) 0.123 (105–150 °C) 0.028 (165–200 °C)
PbTNP	$a = 10.096$ $b = 6.335$ $c = 9.340$	119.807	518.37	5.2×10^{-9}	4.4×10^{-6}	0.262 (30–200 °C)
PbTAP	$a = 8.213$ $b = 7.103$ $c = 7.914$	105.731	444.49	1.1×10^{-6}	1.3×10^{-4}	0.139 (30–125 °C) 0.178 (145–200 °C)

donor amino groups. This may be due to the smaller size of amino group in comparison to the nitro group which is expected to stack the molecule with smaller intermolecular distance resulting greater intermolecular interactions between the molecules. This provides a better pathway for the charge carriers resulting an improved electrical conductivity in the case of PbTAP. The change in energy of activation observed with the different temperature ranges of PbTAP may be due to some phase transformations and variations in the intermolecular interactions.

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