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Synthesis of tetra-diiminobenzene-p-aminobenzene phthalocyaninato metal (III)

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Abstract

The present study includes the synthesis of phthalocyanine compounds with general formula X4PcM where M= Fe (III) and Fe (II), X is a peripheral substitution in the position-4 on the four benzene rings which include NO_2, NH_2 and Schiff base (p-imino phenyl amine). The proposed main compound is tetra-diiminobenzene-p-aminobenzene phthalocyaninato metal. Two kinds of peripheral substitution of phthalocyanine compounds were synthesized, first are planner the other is bridged. The structures of the synthesized compounds were confirmed by elemental analysis, UV-visible, IR and X-ray diffraction techniques. The elemental analysis results showed a good agreement with the theoretical results. The absorption spectra for all compounds showed the characteristic phthalocyanine bands (Q and B bands). In general, the two bands show a clear blue shift for Schiff base phthalocyanine compounds in comparison with the tetra amino phthalocyanine. The infra-red spectra of all compounds were recorded and the spectra of tetraamines derivatives showed two weak bands attributed to the NH_2 groups at the range 3245-3330 cm-1 and 3190-3240 cm^{-1} which are attributed to asymmetric and symmetric stretching vibration respectively. The IR-spectra of Schiff-base compounds show a strong band at the range 1600-1608cm^{-1} corresponding to the C=N stretching vibrations. X-ray diffraction gives the d-spacing (interplanner spacing) of the planes of the crystalline regions which are regarded as the fingerprints for the compounds. In addition, they can be used to calculate the states around Fermi levels during the calculation of α which is regarded as the inverse of the interplanner spacing.

Keywords

Phthalocyanine, schiff base, tetra-diiminobenzene-p-aminobenzene phthalocyanines, x-ray diffraction.

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1. Introduction

The compound that is called phthalocyanine (PC) was first observed as a highly colored product in the chemical reaction of some ortho 1, 2- disubstiuted benzene derivatives [1]. Hindsight prepared metal free phthalocyanine (Pc) and cupper (II) phthalocyanine (PcCu) respectively, phthalocyanines and their metal complexes have been investigated for many years in great details [2]. In grangemouth, Scotland (1928), during the industrial preparation of the phthalicimide from phthalic anhydride and ammonia, phthalocyanine was prepared as a dye, this structure was confirmed later by X-ray diffraction techniques [3].A patent covering the preparation and properties of the phthaloamine was granbed in 1929[4]. Linstead showed that phthalocyanine is a marcocyclic material composed of four isoindol units with central cavity of sufficient size to accommodate various metal ions Linstead initial series of papers contained the experimental details for the preparation of PC's from phthalonitrile (ortho dicyano benzene) which is still the best product for PC synthesis [5, 6]. The central metal atom can carry additional ligands [7]. It was noted that phthalocyanine is closely related to naturally occurring porphrin. The difference being the four-benzo structure and nitrogen atoms at each of the four meso positions [8]. Occasionally phthalocyanine is referred to as tetra-benzoporphrazen or tetra-benzo tetra azo porphyrin [9]. Phthalocyanine was assumed to exhibit aromatic behavior owing to its planner-conjugated array of 18π electrons; as predicated by Huckel theory of aromaticity [10, 11]. Linstead gave the name phthalocyanine as a combination of the prefix phthal (originally from the Greek naphtha rock oil and Greek cyanine (blue) [12]. Formerly, phthalocyanine was mostly used as dyes and catalyst [13]. Lately, phthalocyanine chemistry has been undergoing a revival, because, phthalocyanine and their derivatives exhibit properties that are interested for their applications in material science [14]. Many metallophthalocyanine can be easily synthesized in high yields and purity, and also exhibit a high thermal stability. Metallophthalocyanine containing peripheral substituents on the aromatic rings were synthesized from the corresponding substituted phthalonitriles, phtalic acid and phthalic anhydride [15]. Different types of peripherally substituted phthalocyanines were synthesises, such as, phthalocyaninato iron, cobalt, copper and lead from the reaction of substituted phthalonitriels and metal salts or metal carbonyl [16, 17, 18]. A concept was developed to obtain a stacked arrangement of phthalocyanine coordinated to transitional central metal atoms [19,20], leading to coordination polymers where the macrocycle, the central metal atom and the bridging ligand can be varied systematically, this arrangement is called μ-bridged or stacked phthalocyanine (4). Stacking is achieved by biaxially connecting the central metal atom of the macrocycles with bidentate bridging ligand (L) such as bridged phthalocyanitometal compounds. The bridging ligands (L) are either linear organic molecules containing a conjected π- electron system. e.g. pyrazine (pyz), p-diisocyano benzene (dib) and tatrazine (ta) or oxygen and fluoride (oxo and fluro bridged) [21-22, 23,24 25], Many of the bridged macrocyclic metal complexes [Mac ML]n, such as, [LPcM]n can be synthesized in high yield and purity by treating the metallophthalocyanine (PcM), with pure ligand in an appropriate solvents, e.g. acetone, chloroform and benzene, as an examples $[(PcFe(pyz)]_n$ is obtained as a dark violet solid by the reaction of (PcFe) and pyrazine in benzene or directly by reacting (PcFe) in a melt of pyrazine [26]. The bridging structure has been proved for many compounds using a variety of physical methods including thermogravimetry, IR, 1H and C13-NMR spectroscopy [27, 28].

2. Methods

a- Synthesis of 3 and 4-tetranitrophthalic acid:

Fuming nitric acid was prepared by distillation of a mixture of equal volumes of conc.HNO_3 (Sp.gr.1.42) and conc.H_2SO_4 (Sp.gr.1.834), the first third of the volume was taken as a fuming HNO_3) [29]. A mixture of 42 mL fuming HNO_3, 20 mL conc. H_2SO_4 (Sp.gr.1.834) were poured into a three necked bottomed flask fitted with condenser and mechanical stirrer. A 50g (0.34mol) phthalicanhydride was then added. The mixture was heated on a water bath at 100 °C for 12 hours. The product was cooled and poured into 200 mL water and left for 2 hours. Two layers were formed, the solid layer was filtered and recrystallized with hot water. The product (3-nitrophthalic acid) [1] is yellow crystals with melting point (216-218) °C and yield is 11g (23%). The upper layer was concentrated and left to crystallize. The solid material was filtered and recrystallized with diethyl ether to afford the product (4-nitrophthalic acid) [2] as yellow-white crystals with melting point (162-163)^{0}C. The yield is 31g (62%) [30, 31]. The reaction steps are shown in scheme 1.

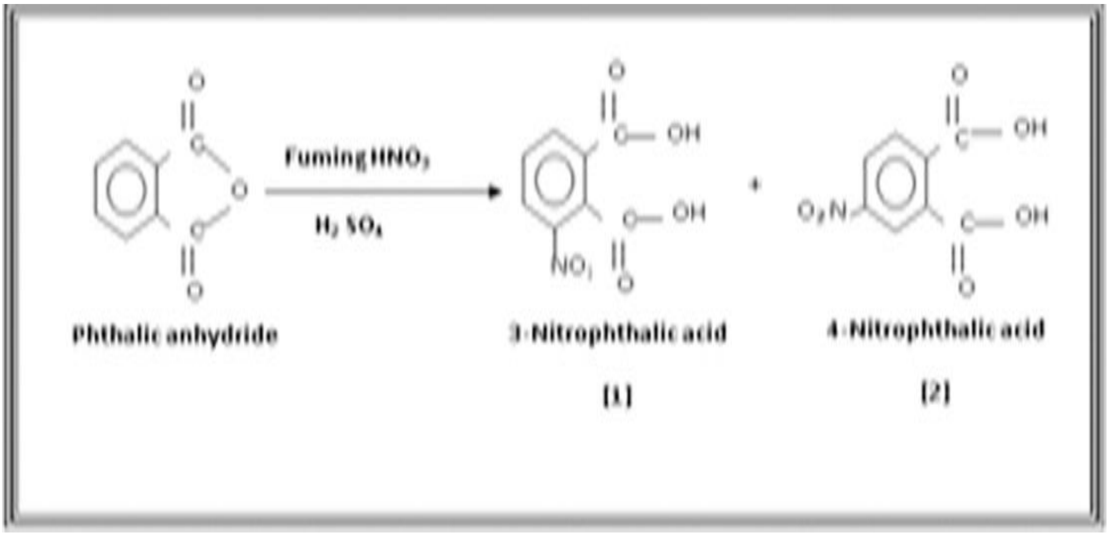

Fig.1- synthesis of 3 and 4 nitro phthalic acid

b- Synthesis of tetranitrophthalocyaninato metal $(NO_2)_4$PcM (II) & (III) [32].

A mixture of 10g Urea, 6.75g (0.032 mol) 4-nitrophthalic acid, and 4g (0.019 mol) $CuSO_4.5H_2O$ and 0.1g ammonium molybdate in 50 mL nitrobenzene was refluxed for 6 hours. The reaction mixture was then cooled and filtered and the crude products were purified by refluxing with 100 mL of 1N of each of HCl and NaOH respectively and then washed with hot water. The solid material recrystallized from DMF and dried at 110^0C. The product (4, 4', 4'', 4'''-tetranitrophthalocyanato cupper (II) [2, 3] was isolated as dark blue powder with yield (82%). The reaction steps are shown in Scheme (2). The compounds of Zn (II), Al (III) and Fe (III) were prepared according to the above procedure. The amounts of the used materials, the physical properties of the products and the yield are shown in Table (1).

c- Synthesis of tetranitrophthalocyaninato Metal (NO2)4PcM (II) & (III) [32].

A mixture of 10g Urea, 6.75g (0.032 mol) 4-nitrophthalic acid, and 4g (0.019 mol) $CuSO_4.5H_2O$ and 0.1g ammonium molybdate in 50 mL nitrobenzene was refluxed for 6 hours. The reaction mixture was then cooled and filtered and the crude products were purified by refluxing with 100 mL of 1N of each of HCl and NaOH respectively and then washed with hot water. The solid material was recrystallized from DMF and dried at 110 °C. The product (4, 4', 4'', 4'''-tetranitrophthalocyanato cupper (II)) [32] is dark blue powder with yield 82%. The reaction steps are shown in Scheme 2. The compounds of Zn (II), Al (III) and Fe (III) were prepared as in the above procedure. The amount of the used materials, the physical properties of the products and the yields are shown in Table (1).

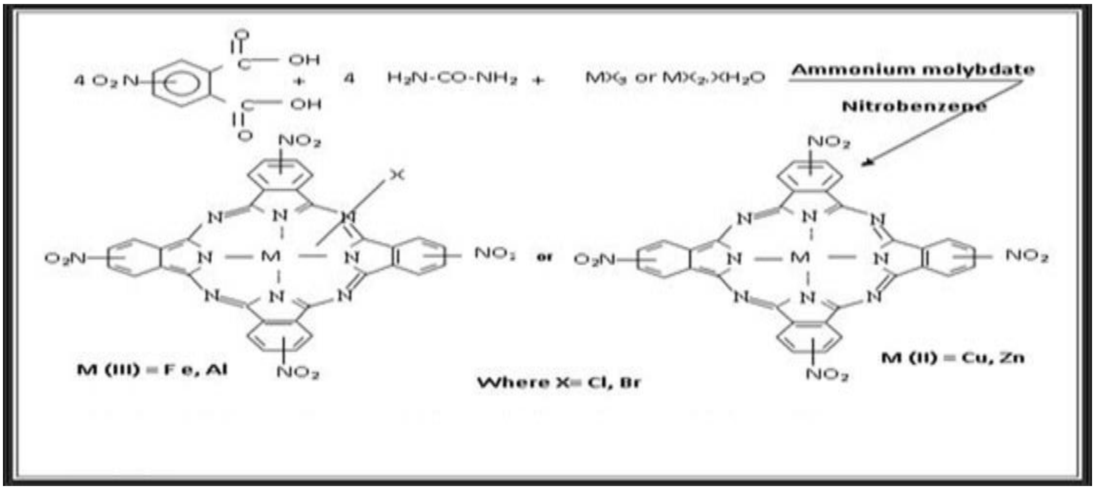

Fig.2- Synthesis rout of tetra nitrophthalocyaninato metal

d- Synthesis of tetraaminophthalocyaninato Metal $(NH_2)_4PcM$ (II) & (III). [33]

A mixture of 4g (0.0053 mol) 4, 4', 4'', 4'''-tetranitrophthalocyanato cupper (II) and 10g (0.041 mol) $Na_2S.9H_2O$ (excess) in 50 mL of water heated with stirring for 12 hours at 60 °C. The reaction mixture was cooled and filtered. The solid product was refluxed with 50mL of solutions of 0.5 N of both NaOH and HCl respectively. The solid product then filtered and washed with hot water and dried at 110 °C. The final product (4, 4', 4'', 4'''-tetraaminophthalocyaninato cupper (II) [6] was isolated as blue powder. The yield is 70%. The reaction steps are shown in scheme 3. The aminophthalocyanine compounds of Zn (II), Fe (III) and Al (III) were synthesized according to the above procedure the amounts of the materials used, the reaction times. The physical properties of the products with the yield are shown in Table (1). The amount of the rest materials, urea, $(NH_4)_2MoO_4$ and 4-nitrophthalic acid were mentioned referring to the first experiment.

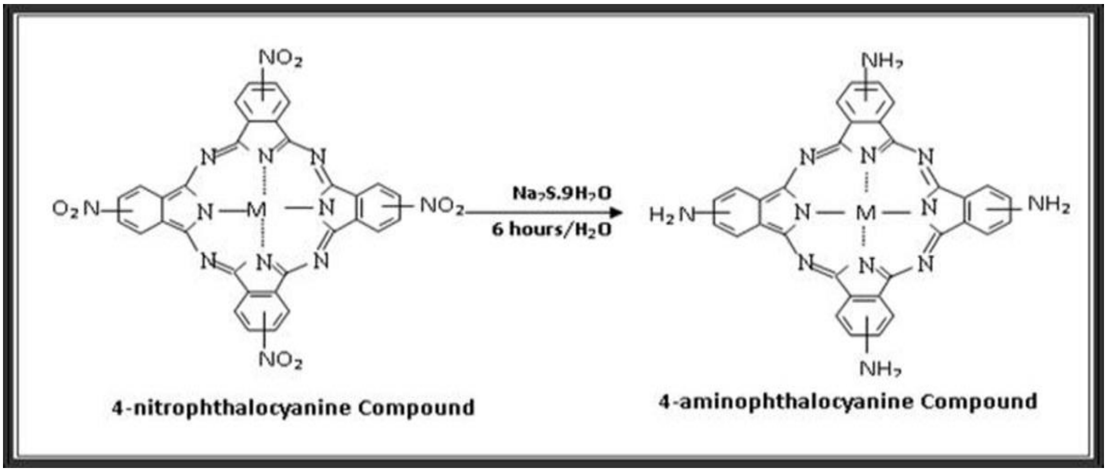

Fig. 3- synthetic route for tetra amino and nitro phthalocyanino metal II and III

e- Synthesis tetra-diiminobenzene-p-aminobenzenephthalocyaninato metal (II), (III) & [II]

A mixture of 4,4',4'',4'''–tetraaminophthalocyaninato cupper(II) (0.656 g, 0.001mole) and 4-acetoamidobenzaldehyde (1.304 g, 0.008 mole) in nitrobenzene (20 mL) and a few drops of HCl were refluxed for 12 hours. The solid product was filtered and purified by refluxing with 50ml of an absolute ethanol to give the solid products (Schiff bases) was filtered. The data of elemental analysis for the synthesized compounds are shown in table (3) and dried at 110 °C. The product is dark black powder and the yield. The reactions are shown in Scheme 4.

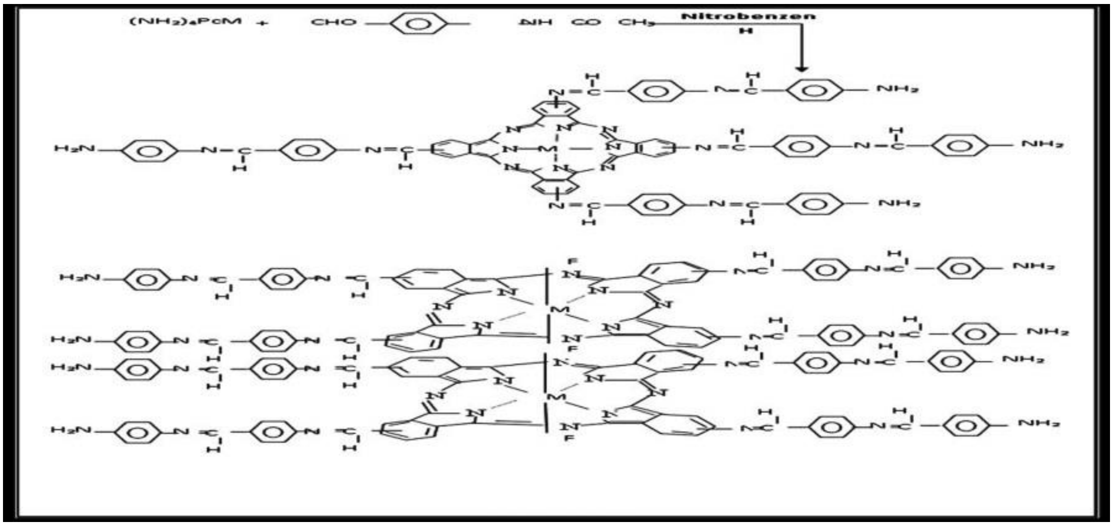

Fig. 4- the synthetic route of the predicted compounds.

Table 1-The conditions of the synthesis of tetra nitrometallo- phthalocyanines.

No	Metal salt	Salt weight	Product color	yield
1	$CuSO_4.5H_2O$	4.00 g (0.019 mol)	Blue powder	82%
2	$ZnSO_4.7H_2O$	5.46 g (0.019mol)	Green powder	80%
3	$FeCl_3$ anhydrous	3.06 g (0.019mol)	Dark green powder	82 %
4	$AlCl_3$ anhydrous	2.50g (0.019mol)	Green powder	82.5%

Table 2- The conditions for the synthesis of tetra- amino metalo phthalocyanines

No	Metal salt	Wt. of nitro compounds	Product color	yield
1	$CuSO_4.5H_2O$	4.00g(0.005mol)	Blue powder	70%
2	$ZnSO_4.7H_2O$	3.79g (0.005mol)	Green powder	68%
3	$FeCl_3$ anhydrous	3.59g(0.005 mol)	Blue powder	66%
4	$AlCl_3$anhydrous	3.73g (0.005 mol)	Dark blue powder	70%

Table 3- The elemental analysis data of the sythesised compounds.

No	Compound	Calculated%			Found%		
		C%	H%	N%	C%	H%	N%
1	Schiff-base (Cu)	71.1	4.91	18.8	71.12	4,88	18,66
2	Schiff-base (Zn)	71.6	4.95	19.0	71.4	4.91	18.8
3	Schiff-base (Al)	72.5	5.01	19.00	72.25	4.93	19.05
4	Schiff-base (Fe)	71.1	4.91	18.8	71.12	4.88	18.66

3. Results and dissuasion

IR spectra:

The IR spectra of the synthesized compounds were recorded on KBr discs. Figure 1: Ir spectrum of Schiff base of PcFeF using KBr disc. Table (4) shows the IR absorption data. Spectrophotometer 14500, with wave number range (3500-400) cm^{-1}.

Table 4- The IR- absorption data of phthalocyanine compounds.

NO	Compound	Frequencies cm^{-1}
1	Tetra amino PcCu	3371w, 3338w, 2960, 1605v, 1492m, 1400w, 1340vs, 1250m, 1135w, 1095s, 1047w, 930w, 850m, 755vs,730m
2	Tetra amino PcZn	3380w, 3340w, 2850, 1603s, 1495w, 1406w, 1340w, 1250w,1135w, 1095s, 1045w, 935w, 725s, 723m
3	Tetra amino PcAl	3410s, 3370s, 2900 1510s, 1300s, 1250w, 1150s, 1100s, 750s, 730, 550s
4	Tetra amino PcFe	3465s, 3410w, 2950, 1500, 1400s, 1360m, 1090s, 750s,570s
5	Schiff base of PcCu	2900s, 2800s, 2500w, 1600s, 1500, 1450, 1300, 1200, 900, 800, 650
6	Schiff base of PcZn	2400s, 1900, 1600, 1500, 1400,1300, 1150, 850, 650
7	Schiff base of PcAlF	2350w, 1600s, 1500s, 1200s, 115os, 1000s, 850s
8	Schiff base of PcAlF	3100s, 1600s, 1500s, 1400, 1300, 1200, 1150s, 910,840,690

Table (4) shows general features of the IR spectra of amino and Schiff base derivatives of phthalocyanine compounds [3]. The amino derivatives show the main IR bands, which include –N-H symmetric and asymmetric stretching vibration at 3290-3190 cm^{-1} and –N-H bending at 1617 cm^{-1}, in addition to the C-H stretching vibration at 2960-2850 cm^{-1} and C-H bending at 1310 cm^{-1}. The ir figures and table (4) show the C=N stretching vibration r the imino group of the Schiff base at 1600-1608 cm^{-1} as a new band as compared to the spectra of amino derivatives. These compounds show the N-H stretching vibration at 3389-3410cm^{-1}of amino group and the C-H stretching for imino group at 2900-2350 cm^{-1} [34]. Furthermore, AAn expected weak band at 500-200 cm^{-1} is attributed to carbon metal stretching vibration, which is difficult to be identified due to the crowded region 3.

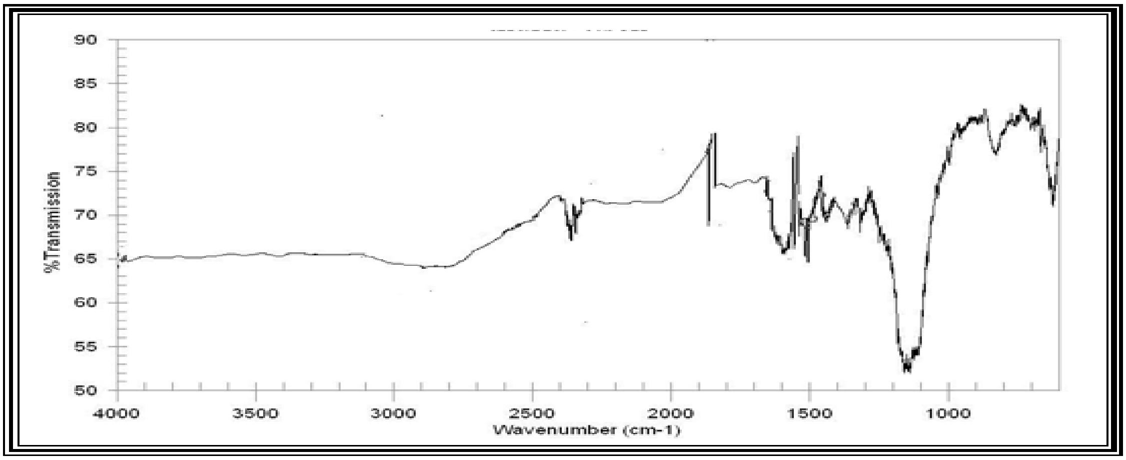

Fig. 1- A typical IR-spectrum of Schiff base of PcZn using KBr disc

Electronic spectra:

The UV-visible electronic spectra were recorded in the range (200-800) nm using L.R1156 Spectrophotometer. The spectra of the synthesized compounds were recorded in DMF, using 1cm quartz cell at (25 -28) ^{0}C. The measurements were carried out at Physics Department/ College of Science/ Basrah**.**

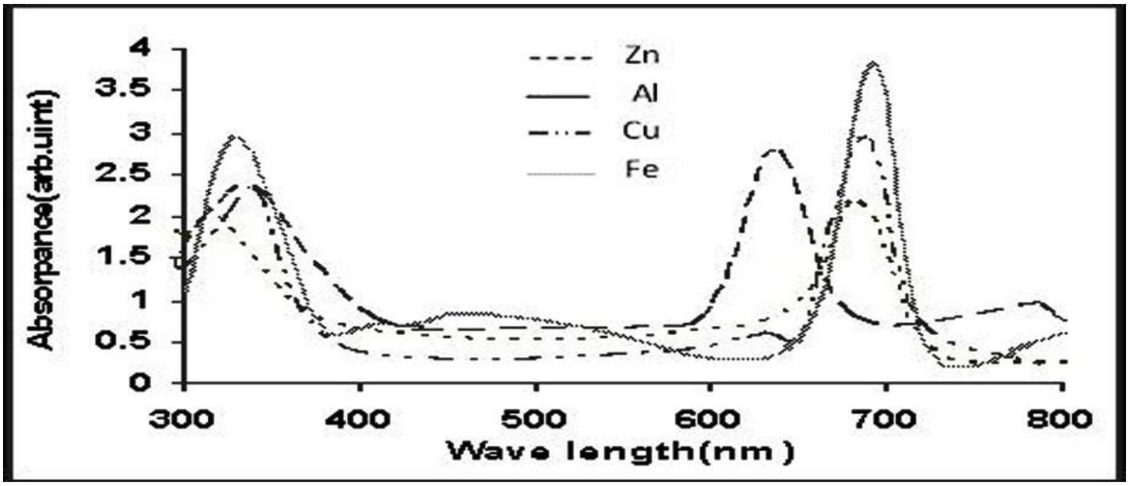

Fig. 2- Electronic spectra of Schiff bases for metallophthalocyanines.

Figure 2 shows a typical electronic spectrum for the synthesized compounds. All the spectra show the general features of spectra of phthalocyanines compounds with two main peaks at (637-734) nm (Soret-band) and (320-460) nm (B-band) (sort band) [3]. All electronic spectra show a blue shift of both bands position on going from amino phthalocyanine to the Schiff base of phthalocyanine as summarized in Table (5).

Table 5- The absorption bands for the synthesized Schiff bases.

Compound	**Q bands**	**B bands**
$(NH_2)_4PcCu$ Schiff-base (Cu)	460 329	734 690
$[(NH_2)_4PcFe]n$ Schiff-base (Fe	367 320	720 682
$(NH_2)_4PcCu$ Schiff-base (Cu)	378 340	723 687
$(NH_2)_4PcZn$ Schiff-base (Zn)	328 338	700 637

X-ray diffraction:

The X-ray diffraction measurements were recorded using PW-1320 X-ray diffractometer at Physics Department/ College of Science/ Basrah. Figure 3 shows typical powder x-ray diffraction spectra. All x-ray patterns show some crystalline nature of the solid powder of the compounds. Table (6) shows the calculated interplanner spacing of the crystal regions of the Schiff bases as collected from the figures using Brags law ($n\lambda=2d \sin \theta$), where n is a constant, λ is the wavelength of the Cuk_α source which equal to 1.54 Å, d is the interplanner space and θ is Brags angle which is the angle between the incident beams and the diffracted beam, the table shows that the interplanner spacing ranges are (4.03-2.59) Å, for the prepared Schiff base phthalocyanine compounds. Table (7) shows the interplanner spacing for the highest peaks and their inverse values for the synthesised compounds [25].

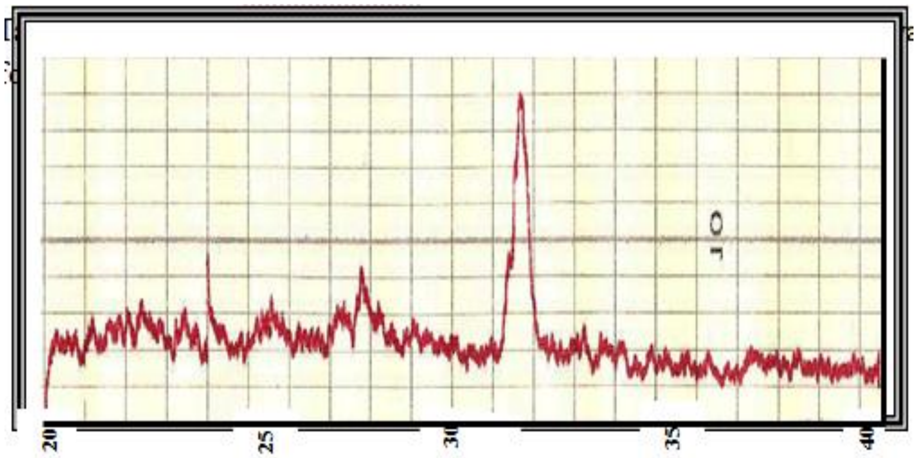

Figure 3: A typical X-ray diffraction pattern for Schiff PcAlF.

Table 6- The inter planner spacing of the synthesized Schiff bases as taken from the figures.

NO	Compound	Peaks (Å) (Q converted by Brag's law to d in Å
1	Schiff base PcCu (II)	4.035, 3.5229, 3.04, 2.88
2	Schiff base PcZn (II)	037, 3.2217, 2.815
3	Schiff base PcAlF (III)	3.02, 2.8817, 2.5969

Table 7- The interplanner spacing of the highest peaks and its inverse (α) for the synthesizes Schiff bases.

NO	Compound	d(Å)	A
1	Schiff base PcCu (II)	4.035	0.2477
2	Schiff base PcZn (II)	3.7037	0.2700
3	Schiff base PcAlF (III)	3.0200	0.3310
4	Schiff base PcFeF (III)	3.7037	0.2700

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