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Synthesis and characterization Of Bridged phthalocyanine & tetra pyrazino Porphyrazine complexes of Iron(III) and their copolymer

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Abstract :

A two types of bridged complexes of Iron (III) with two types of ligands phthalocynine & tetrapyrazino Porphrazine were prepared according to adjusted procedure as in the litratures to forms a two complexes , Phthalocyanina to separately Iron(III) chloride[I] and tetrapyrazino Porphrazine iron (III) chloride[II] were converted to phthalocyanato Iron(III) hydroxide [III] and tetrapyrazino Porphrazine Iron(III) hydroxide[IV] separately. The hydroxide complexes then converted to the bridged polymeric fluoride complexes [V] and [VI] .The copolymer [VII] were prepared from the mixed of hydroxide complexes [III] and [IV] of(1:1) ratio to the polymeric fluoride of two ligands .The compounds then characterized by elemental analysis and spectroscopic methods.

Keywords : Bridged Iron(III) phthalocynita and tetrapyrazino Porphrazine complexes Abridged copolymer.

Introduction :

Tetra azaporphrazin or, porphyrazines[1] are part of a family from aromatic compounds . The tetrapyrrolic ring system can be divided into two distinct categories , namely porphyrins and tetra azaporphyrins , in which meso nitrogen atoms replace the methin groups .

The later category is further divided into porphyrazines (Pc) [2],and phthalocyanines(pz) , which contains benzanoid rings fused with macro cyclic periphery. The compound has electronic and optical properties.

In recent years porphyrazines that bear a ring containing hetroatomic substituents were studied.

The compounds have Potential application include biomedical agents chemical sensors , liquid crystals , non-linear optics , Langmuir –Blodgett films , and ladder polymers[3] bridge polymer

It was found a strong correlation between the nature of the substituent and optical properties[4]of the macro cyclic ring system. In comparison to the other family members , analogous derivatives are virtually inaccessible for the porphyrins , A direct fusion of hetroatomic substituent onto the porphyrazine β - Position[5] result in a pronounced effect compared with the substitution of an equivalent group onto the benzenoid rings of the phthalocyanine , The poryrazines display a vastly increased solubility in organic solvents compared with their phthalocyanine counterparts . Thus , porphyrazines[6] maintain a unique position in the family of tetrapyrrolic macrocycles , and their straight forward synthesis , coupled with their tunable electronic and optical properties , renders them exciting candidates for a whole range of application.[7]

Fluorine may act a bridging ligand between two metal some complex molecules. Molecules containing fluorine may also exhibit hydrogen bonding , a weak bridging with link to certain nonmetals . new concept was developed to obtain a stacked arrangement of phthalocyanine coordinated to transition center metal atom leading to coordination polymers were the macro cycle.(1,3)

Experimental.

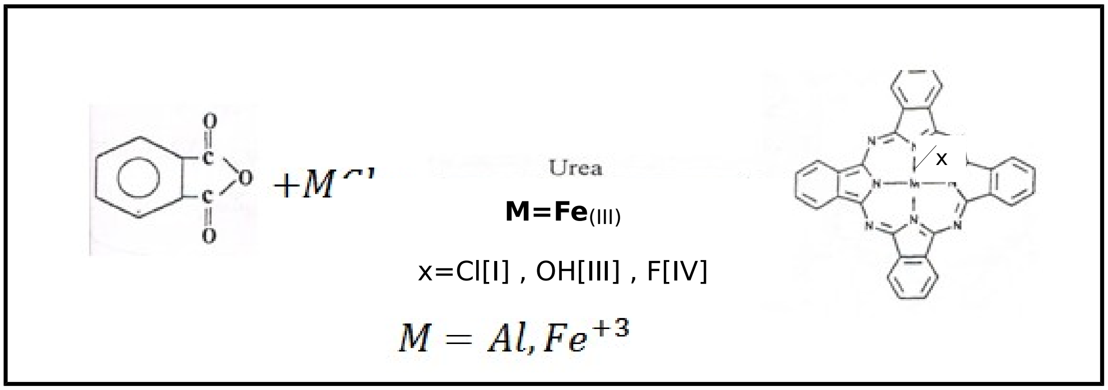
A: Chemical Materials.

The chemicals were used as they were supplied except pyridine and quinoline were distilled twice for each.

i. Synthesis of phthelocynine compounds.

Phthelocynine Iron chloride . FePcCl: [I]

A mixture of phthalic anhydride(4.5g, 0.04mol)[8][9], Iron (III)chloride (1.33g, 0.01mol) , urea (8g) , ammonium molbadat (0.01g) , nitro benzene(50mL) was refluxed for 5 hours the reaction mixture was cooled then filtered and washed with Ethanol , acetone and CCl_4 , The crude reaction products were purified by reflux with (100mL) of 1N of each HCl and NaOH final wash was done with hot water and dried at 110C° yield (3g 68%). The product (FePcCl) is dark blue powder.



Phthelocyninato Iron fluoride.(FePcf)$_n$ [V]

A mixture of FePcCl (1.5g), ammonium hydroxide 25mL (25%) and pyridine(50mL) was refluxed for 7 hours . The resulting solid was filtered , washed with conc ammonium hydroxide and water then it was dried at 110C°. Aportin of this product (1g) was evaporated to dryness on a steam bath with three separate portions of (40%) hydro fluoric acid(20mL each 15minute). The resulting solid was washed with water acetone, and dried at 110C° .The yield was formed(0.9g 62%) of $(PcFeF)_n$ the product is dark green powder. The elemental analysis C.H.N.of $(C_{32}H_{16}N_8FeF)_n$, calculated C:65.41 , H: 2.72 , N: 19.08 ; Found C:65.40 H: 3.4 , N: 19.02.

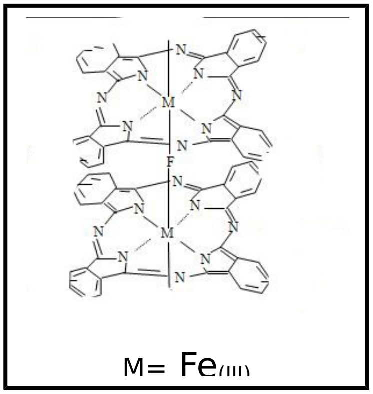


Figure (2) : Synthesis of (PcFef)n

ii .Synthesis of porphyrazine.compounds.
Synthesis of 2,3-dicyano pyrazine [10]. (PN)
(1mL) of glyoxal was dissolved in 25 mL ethanol and 25 mL of acetic acid and then the mixture was added into conical flask connected with condenser contain (2.36g, 0.0218 mol) of diamino malonetrile (DAMN) which was dissolved in 25 mL ethanol .The mixure then was refluxed for 4 hours and then left for two day to settle down ,the price pated then filtered and recrystallized from mixture of hexane and acetone(1:1) ratio. The yield 2,3-dicyano pyrazine was (0.73 , 35%) and the physical state is dark brown powder.

Figure (3) : Synthesis of (PN)

Preparation of tetra pyrazino porphyrazine iron (III) chloride (FePzCl).[II]

Amixture of iron (III) chloride anhydrous (0.133g , 8 $x10^{-4}$ mol) , 2,3- dicyano pyrazine (1.12g , $4x10^{-3}$mol), Urea (1.5g, 4.5 $x10^{-4}$mol), 8 mL quinoline was refluxed for 4 hours. The reaction mixture was left out all the solvent was evaporated. The crude reaction product were purified by dissolving in chloroform $CHCl_3$, then added dropwise a Buker continues ethanol .The precipitate filtered then dried at 110C° The yield (0.26g 63%) of (FePz Cl) is dark brown powder.

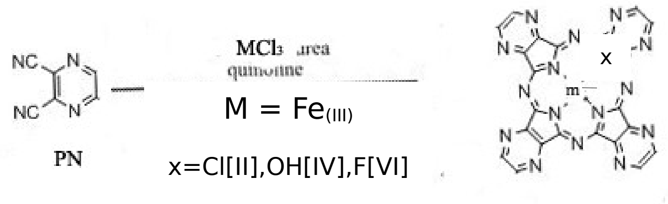


Figure (4)) : Synthesis of (FePz Cl)

Synthesis of tetra pyrazino porphyrazine iron(III) Fluoride (Fe PzF)$_n$ [VI]
A mixture of (FePzF) (1.5g, 2.5 x10^{-3}mol), ammonium hydroxide 25 mL (25%) and pyridine 50 mL were refluxed for 7 hours .The resulting solid were filtered , washed with conc ammonium hydroxide and hot water then it was dried at 110C°. A portion of this product (1g) was evaporated to dryness on a steam bath with three separate portions of 40% hydro fluoric acid (20mL each tim) , The solid product was dried at 110C° .The yield was formed to be (0.85g , 60%) of (FePzF)$_n$ them.
The element analysis CHN :Calculated ($C_{24}H_8N_{16}FeF$)$_n$ C: 48.40 , H: 1.34 , N: 37.64 Found : C: 48.90 , H : 1.68, N: 37.08.

F

M=Fe(III

Figure (5) : Synthesis of (Fe

iii . synthesi of (1:1) molar ratio of (FePcF-FePzF)$_n$[11 II]

A mixture of Fe Pc OH. (0.5g, 0.001mol) and FePzOH. (0.5g, 0.001mol) was evaporated to dryness on a steam hydrofluoric acid (1 mL each time) .The resulting solid was washed with acetone ,water and dried at 110C°.The Yield (0.45g) of (PcfeF-FePzF).

CHN :Calculate $(PcfeF\text{-}FePzF)_n$ C: 56.85 , H: 2.03 , N: 28.42 ; found: C: 65.19,H:1.70 N:28.00

F

Figure (6) : Synthesis of$(FePzF)_n$

Result and Discussion.

Infra-Red spectra(FT-I.R)

The IR data of these complexes display characteristic bands for the functions groups at certain frequencies , Figure(7-9) show the IR spectra of the polymer and copolymer respectively while table(1) summarizes the important vibration bands of the prepared complex .The observed vibration bands are similar to these in the literature and typical reprehensive of IR spectra for compounds.

The IR spectra show a strong band in the range (1400-1660)cm^{-1} due to (C=C)[12] stretching, while (C = N) appear in the range(1637-1724cm^{-1}) .

The aromatic C-H stretching band broad appeared in range(3045-3186)cm^{-1}. The bonds in the range (600-640cm^{-1}) which might be attributed to the stretching vibration of the(M-F) band.These band refer to the bridging structures of these polymer.

Table (1) The I.R- absorption data for the prepared complex

Compounds	C-H (st)	C = C (st)	C = N (st)	C-N (st)	AL-F (st)	$C\text{-}H_{ben}$	
						Out of plane	In the plane

(Fe PCF)n	3045	1400 1465	1724	1300	640	797	1081 1120
(FePzf)n	3186	1402	1651	1300	590	746	1083
Copolymer (Fe PCF -FePzf)n	3186	1600	1637	1334	600	725	1083 1120

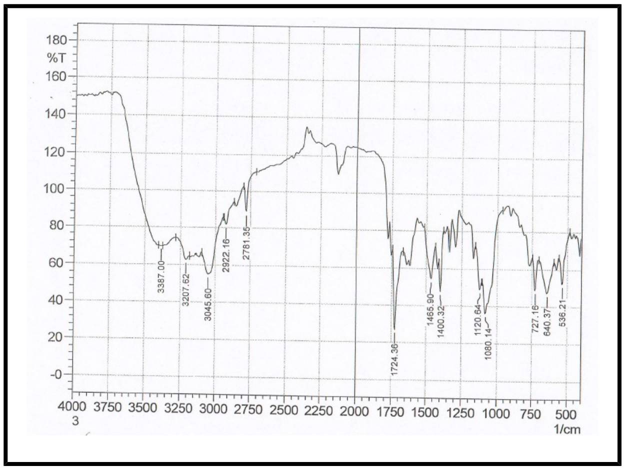


Figure (7): IR $(FePCF)_n$

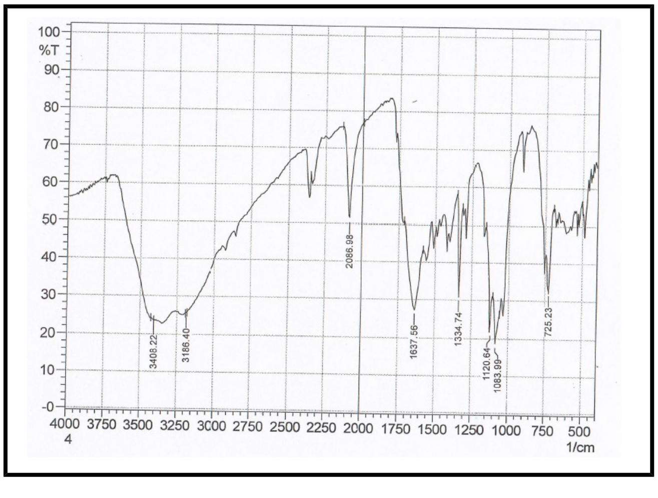


Figure (8) :IR $(FePzF)_n$

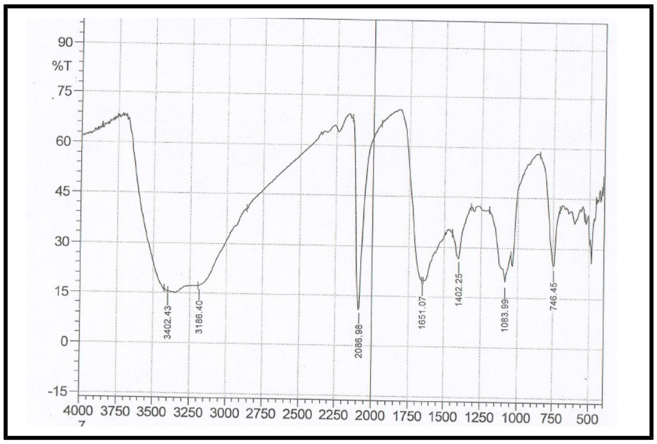


Figure (9) : IR Copolymer of $(FePCF\text{- }FePzF)_n$

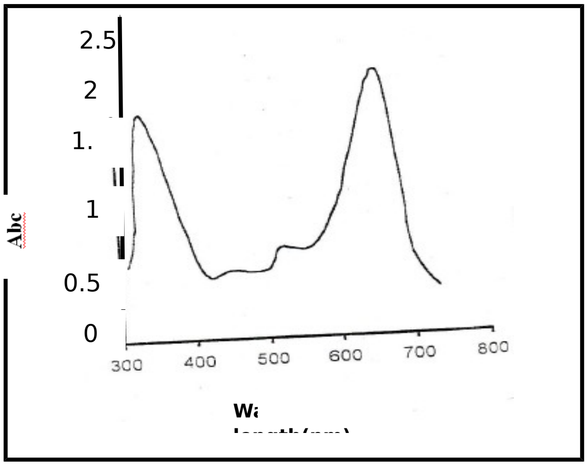
3. Electronic spectra

The UV-Visible data of all prepared complex are measured in the range (200-800nm) using DMSO as solvent. They are summarized in the table(2) ,two electronic transitions are observed in all spectra ,the first transition was observed in the range of (610-665nm) which attributed to a Q-band . The second band which observed in the rang(315-340nm) can be attributed to a B-band or Sort-band . These bands are attributed to (π - π^*) [13][14] and (n- π^*) transition which belong to the hetro-aromatic system of the phthalocyanine and tetrapyarazino porphyrazine molecules.

Table (2): The absorption bands to the prepared compounds

Compounds	Q-band nm	B-band nm
Fe Pc Cl	655	340
(FePCF)n	660	315

Fe PzCl	650	315
(FePzF)n	665	330
Copolymer (FePcF-FePzF)n	610	320



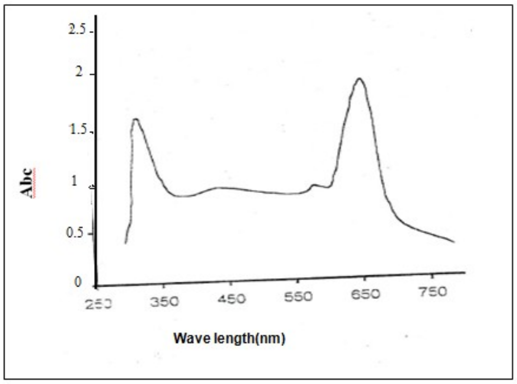


Figure (11) : UV.visible of (FePCF)n

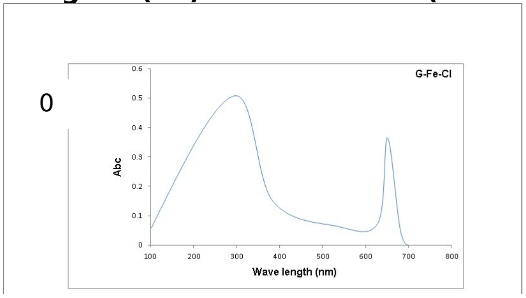


Figure (12) UV.visible of Fe P_zCl

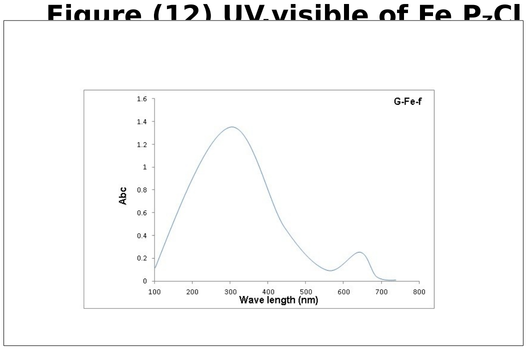


Figure (13) : UV.visible of $(FeP_ZF)n$

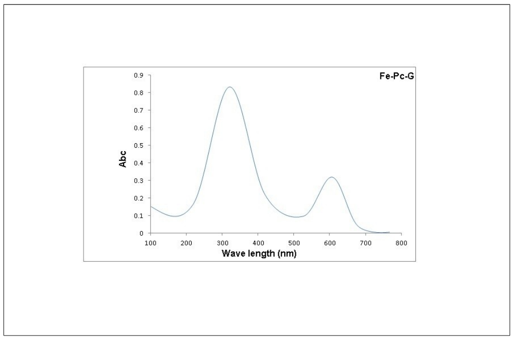


Figure (14) : UV.visible of Copolymer

4. ^{1}H-NMR spectra.

The ^{1}H-NMR spectra of the phthalocyanine and tetrapyrazino porphyrazine provided a characteristic chemical shifts for the prepared complex .$(FePzf)_n$ and copolymer Three peals are clearly seen 7.35 33ppm, 7.4 33ppm, 7.58 ppm which could be related aromatic proton.

^{1}H-NMR spectra show the DMSO absorption which shows a peaks at 0.004ppm 0.83ppm , 2.23ppm , 2.31ppm , 2.49ppm , 2.77ppm , 3.33ppm , 3.39ppm and 4.09 ppm and peaks for the trace of water molecular at 5.4833ppm , 6.1333ppm , 8.2633ppm ,9.3233ppm respectively.[15]

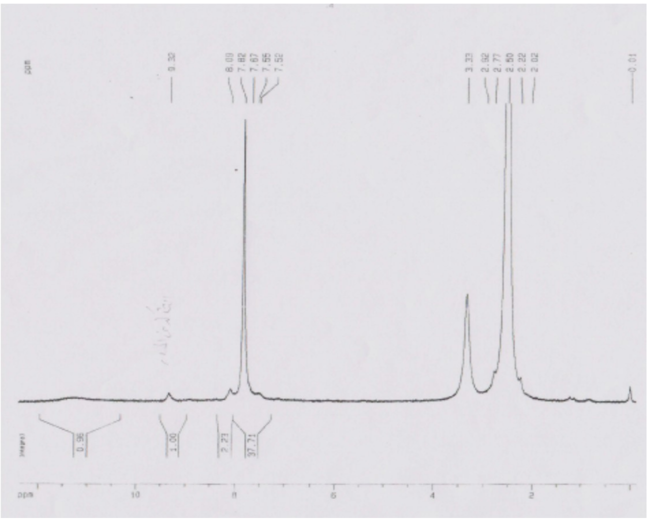


Figure (15) : ^{1}H-NMR spectra of (Fe PcF $)_n$

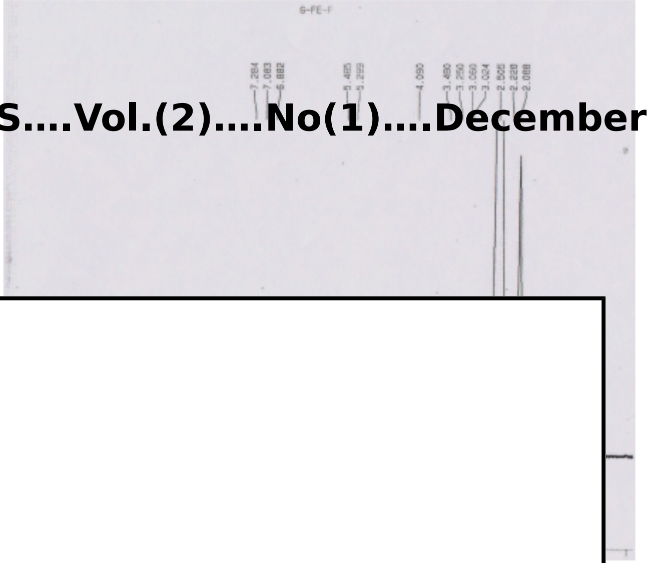


Figure (16) : H-NMR spec

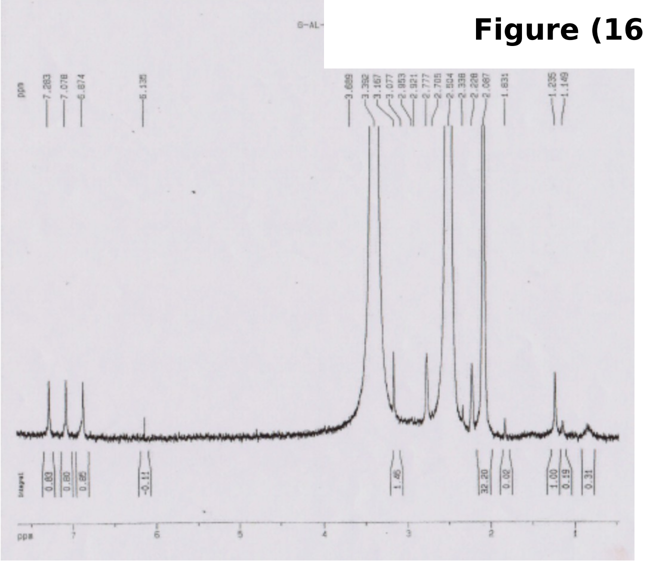


Figure (17): H-NMR spectra of copolymer

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ملخص البحث:

يتضمن البحث تحضير نوعين من المعقدات البوليمرية الجسرية للحديد الثلاثي مع مجموعتين الفثالوسيانين ورباعي البايرازين البورافرازين ، كما حضر البوليمر المشترك لهذه المعقدات. وشخصت هذه البوليمرات المعقدة بالتحليل العنصري الدقيق والطرق الطيفية المختلفة ،(تحت الحمراء ، المرئية وفوق البنفسجية ، والرنين النووي المغناطيسي).