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RESEARCH ARTICLE

PREPARATION OF (PHTHALCYANINATO) BIS (4-METHYLPYRTDTNE) IRON(II) AND STUDY OF IT'SSPECTROSCOPIC AND STRUCTURAL PROPERTIES.

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Manuscript Info *Abstract*

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Bis adduct of phthalocyaninatoiron (II) with 4-methylpyridine was prepared and characterized. The effect of axially coordinated 4-methylpyridine on the spectroscopic and structural properties were investigated, mainly by UV-visible. IR and fast atom bombardment mass (FAB*) In addition the crystal structure was studied by the X-ray powder diffraction technique.

Introduction:-

The reaction between some metallopthalocyanineMPc (M=Co, Fe, Ru,...) with coordinated bases pyridine , pyrazine , tetr:azine and other's gives either mono or bis adduct depending on the metal, temperature , time of reaction , steric and electronic properties of the base(1-4), This paper investigates the effect of the adduct (4-methylpyidine) the spectroscopic- and structural properties of the phthalocynainatoiron (II)

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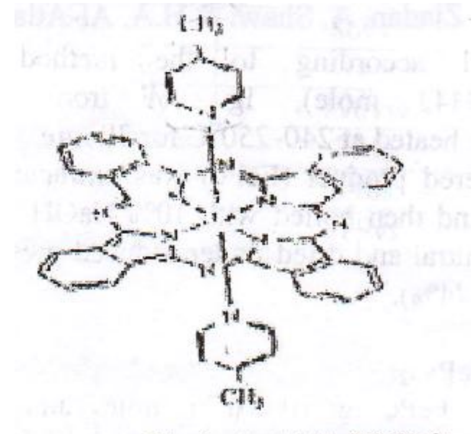

Fig.1 FePc(4-MePy)$_2$

Preparation of o- cyanobenzamide:-

O-cyanobenzamide was prepared according to the method of Lowery et.al"(5) 20 g. (O.136 mol) of Phthalimide was stirred with 100 ml (excess) of conc. Ammonium hydroxide (25%) for 24 hours at room temperature. The produced Phthalimide was then filtrated off washed with water and ethanol, and dried at 100C, (yield 20.75g.,,,93%).

A mixture of phthalamidel6g. (0.0975 mole), acetic anhydride 60 ml and 10ml of acetic acid was refuxed for 45 min. and the resultant solution was filtered and the filtrate allowed to cool to 40C and then re-foltred.The solid product (ocyanobenzinmide) was washed with acetic acid, water and re-crystallized from ethanol and dried at 110"C for 24 hours (yield 6.5 g., 45.6%),m.p. 170-171 C,,lit. 172C (5).

Preparation of FePc:-

FePc was prepare according to the method of Barrett et.a1.(6) o-cyanobenzamide 5g (0.0342 mole),1g, of iron filing and 10g of naphthalenel. Were heated at 240-250C for 30 min.

The dark blue powdered product (FePc) was extracted with boiling acetone, filtered (while it is hot) , and then boiled with 10% NaoH , washed with hot water until the filtrate became neutral and dried under reduced pressure (0.01 ton) for four hours at 800C. (yield 3,6g.,74%).

Preparation of PcFe (4-MePy)2:-

A suspension of FePclg . (0.00176 mole) and 4-methylpyridine l5ml (excess) was heated under reflux for 1 hour, and then filtered while it is hot to remove the uncreated FePc. The solution was allowed to cool and then filtered ' The blue solid product was washed with diethyl ether and dried under reduced pressure (0,01 ton) for two hours at 300C (yield 0.939., 7A%).

Results and Discussion:-

Uv=Visible : Electronic spectra were recorded on PyeUnicam SP8-100 spectrophotometer. The electronic absorption spectra of PcFe(4-MePy)$_2$ and FePc exhibit some similarities as shown in Table 1. Both compounds show the characteristic Q and B bands. The band at 415 nm in PcFe (4-MePy)z spectra in both DMF and Cl$_2$B are attributed to metal →ligand charge transfer t(7).

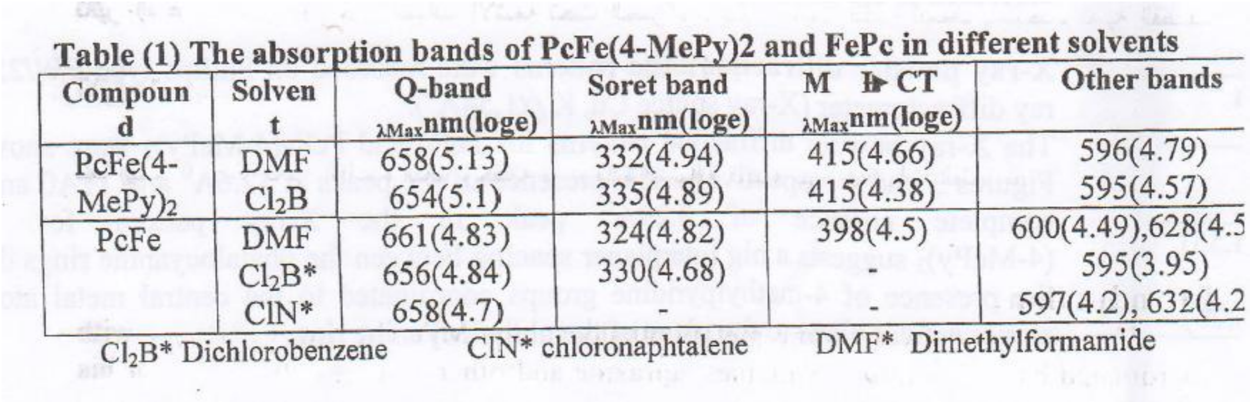

Table (1) The absorption bands of PcFe(4-MePy)2 and FePc in different solvents

Compound	Solvent	Q-band λ_{Max}nm(loge)	Soret band λ_{Max}nm(loge)	M → CT λ_{Max}nm(loge)	Other bands
PcFe(4-MePy)$_2$	DMF	658(5.13)	332(4.94)	415(4.66)	596(4.79)
	Cl$_2$B	654(5.1)	335(4.89)	415(4.38)	595(4.57)
PcFe	DMF	661(4.83)	324(4.82)	398(4.5)	600(4.49),628(4.5
	Cl$_2$B*	656(4.84)	330(4.68)	-	595(3.95)
	ClN*	658(4.7)	-	-	597(4.2), 632(4.2

Cl$_2$B* Dichlorobenzene ClN* chloronaphtalene DMF* Dimethylformamide

Infra-Red:- The IR spectra were recorded on shimadzu 470 spectrophotometer. The main different between the spectra of the parent and the adduct complex are the bands which attributed to the 4-methylpyridine moiety where the CH$_3$ groups of the adduct shows the asymmetric and symmetric C-H stretching at2910 and2840 cm^{-1}(8) . There also some other changes in the other bands of the phthalocyanine complexes(Position and intensity) relative to FePc(9) as shown Table 2.

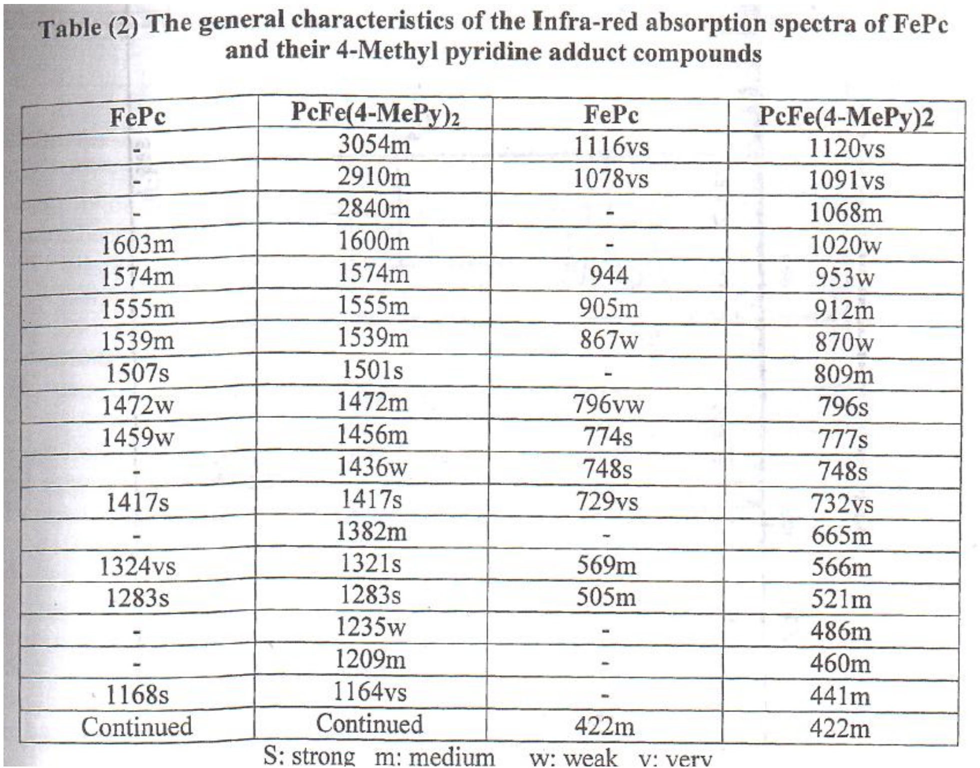

Table (2) The general characteristics of the Infra-red absorption spectra of FePc and their 4-Methyl pyridine adduct compounds

FePc	PcFe(4-MePy)$_2$	FePc	PcFe(4-MePy)2
-	3054m	1116vs	1120vs
-	2910m	1078vs	1091vs
-	2840m	-	1068m
1603m	1600m	-	1020w
1574m	1574m	944	953w
1555m	1555m	905m	912m
1539m	1539m	867w	870w
1507s	1501s	-	809m
1472w	1472m	796vw	796s
1459w	1456m	774s	777s
-	1436w	748s	748s
1417s	1417s	729vs	732vs
-	1382m	-	665m
1324vs	1321s	569m	566m
1283s	1283s	505m	521m
-	1235w	-	486m
-	1209m	-	460m
1168s	1164vs	-	441m
Continued	Continued	422m	422m

S: strong m: medium w: weak v: very

Mass Spectrum:- The (FAB$^+$) mass spectrum was recorded on Finnigan MAT-711A spectrometer, using o-nitrobenzylalcohole (NBA) as a matrix.

The spectrum (Fig.2) possesses a molecular ion M$^+$ at m/z 754 with relative abundance 2.5 and the peak atm/2661.4 with relative abundance 5.2 which attributed to [M- (4-MePy)]$^+$. The high relative abundance 89 at m/z 567.9is attributed to [M-(4MePy)$_2$]$^+$, which reflect the high stability of [PcFe]$^+$. The peaks at 306, 460,6!3 arc attributed to the matrix (NBA1t"r'

X-ray powder diffraction:- The patterns were recorded on Philips type PW253(X ray diffractometer (X-ray source Cu; K&l.54A).

The X-ray powder diffraction patterns for FePc and PcFe(4-M.ty)$_2$ were shown in Figures 3 and 4 respectively, The presence of the peaks at 12.6A0 and 1lA0 and the complete absence of 3.29A peak in the X-ray pattern for suggests a big interplaner spacing between the phatalocyanine rings due to the presence of 4-methylpyridine groups coordinated to the central metal atom in perpendicular plane to the plane of the phthalocyanine ring

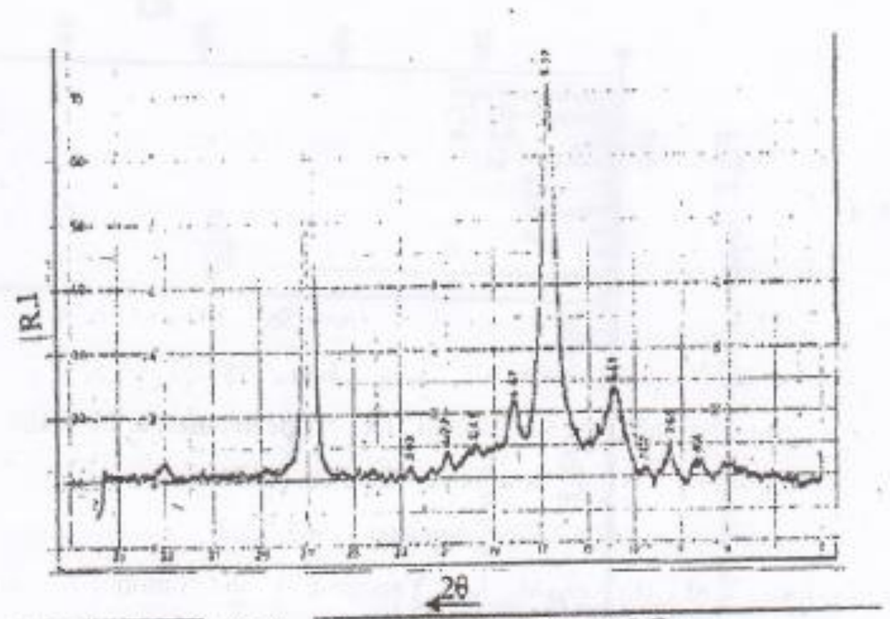

Fig.3 X-ray diffraction pattern for PcFe

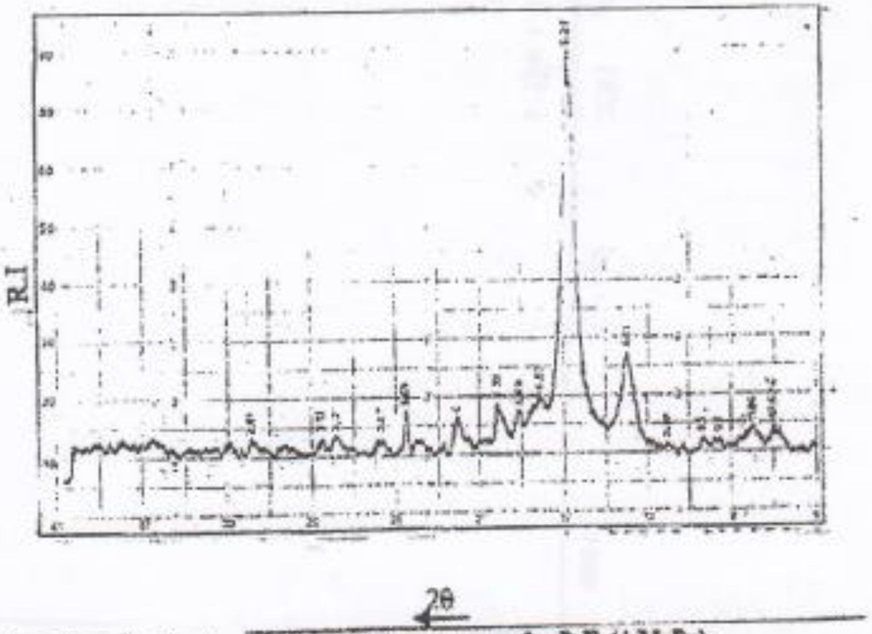

Fig.4 X-ray diffraction pattern for PcFe(4-MePy)$_2$

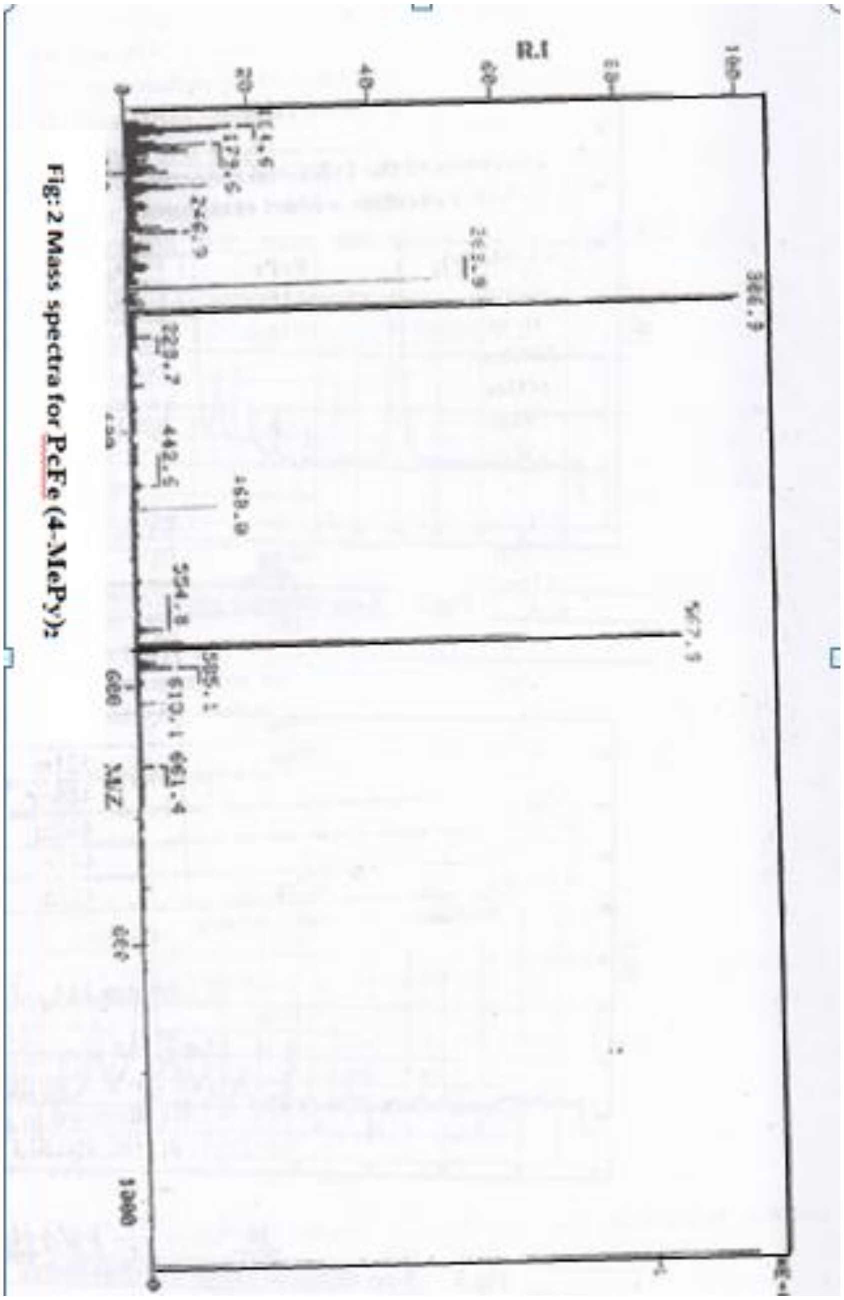

Fig: 2 Mass spectra for PcFe (4-MePy)2

References:-

1. Hanack,M.;Deger,S'andLange,A;Coord,Chern'Rev"1980,83,115.
2. Cariati,F.:andMicera,G':SpectrochimicaActa.;1980,36A,867.
3. Cariati, F.: and Micera, G.; Zoroadu, M.A and Morazzoni, F' :J.C.S. Datton.535 (1e81).
4. Canari,F.; Morazzoni, F. and Busetto .C.J.C.S., Dalton , 496 (1976).
5. Lowery, M.K; Starshok , A. J. ; John, S.J.; Krueqer. P'C,' and Kenney. M'E: Inorg. Chem., 1965,4,128.
6. Barrett,P.A.;Deirt,C.E.andLinstead,R'P':J'Chem'Soc,1936,l719.
7. Metz,J.;Schneider,O.andHanack,M':Inorg'Chem"1984,23,1065.
8. Silverstein, R.M.; Bassler,G.C.and Morrill, T.C. "spectrometric Identification of Organic Coffi6irnds", Wiley, New York' Third ed' (1974)'
9. Lever A.B.P,: Adv .Inorg.chem.Radio chemistry, 1965'7'27 '
10. Nigrimoviskii, V.M.;Bouvel, M.; LukYanets, E.A., and Simon, J.: Journal of porphrins and phthalcyanines, 2000,4,248 .