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ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 1019–1025
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Synthesis, spectral, magnetic and thermal studies on symmetrically substituted metal(II)-1,3,8,10,15,17,22,24-octafluorophthalocyanines

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Received 24 November 2006; received in revised form 3 May 2007; accepted 7 May 2007

Abstract

This publication discuss the synthesis and characterization of pure 1,3,8,10,15,17,22,24-octafluorophthalocyanines of copper(II), cobalt(II), nickel(II) and zinc(II). The complexes are characterized by elemental analysis, electronic spectra, IR spectra, thermal studies and X-ray powder diffraction method to check the purity and integrity of the complexes. The magnetic measurements over the range of magnetic field strength 1.03–2.32 kG showed a variation of magnetic moments with field strength indicating the presence of intermolecular co-operative effect.

Keywords: Phthalocyanines; Octafluoro-substituted; Electronic; IR; Magnetic; XRD; Thermal

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1. Introduction

The monomeric species of phthalocyanines have been mass-produced and used extensively in fields such as paints, pigments, deodorants, charge generation materials in photocopiers, optical disks, removal sulfur from oils and photodynamic therapy of cancer [1,2]. The attractiveness of phthalocyanines may be the versatility of chromophores and relatively easily control of the size and symmetry of monomeric structures, so that these monomers can be used as building blocks in the synthesis of oligomers. Their interaction can be pursued by various spectroscopists, and in addition, many kinds of central metals can be inserted. With the development of laser technology and computer assisted analysis, the level of theoretical and experimental studies has been heightened over the past 15 years, and today studies on even excited states can also be achieved with high accuracy [3].

The phthalocyanines are the second most important colorants and copper phthalocyanine is the single largest-volume colorant sold. Traditional uses of phthalocyanine colorants are as blue and green pigments for automotive paints and printing inks and as blue/cyan dyes for textile and papers [4]. The phthalocyanines are limited to blue/green colors. However, the absorptions can be pushed into near-IR region by the appropriate substitution at the periphery of the phthalocyanine ring and by varying central metal atom. Both these substitution influences the cyclic 16-atom 18-π electron pathway, which is the chromogen.

The literature survey revealed methods for the synthesis of hexadecachloro-, hexadecabromo-, hexadecaiodo- and mixed halogen-substituted metal phthalocyanines and those pigments mainly used for commercial purposes (first part of Ref. [1]). Most of the synthetic methods are patented and hence are not readily available for the researchers. However, there is one reported method for the synthesis of copperoctafluorophthalocyanine and copperhexadecafluorophthalocyanines [5], where in the peripheral substitution of fluorine and method followed are different. Keeping the above facts in mind we have undertaken the synthesis and characterization of 1,3,8,10,15,17,22,24-octafluoro-substituted phthalocyanines of Cu(II), Co(II), Ni(II) and Zn(II).

The present paper discusses the synthesis and structural investigations on substituted metal(II)-1,3,8,10,15,17,22,24-octafluorophthalocyanines. The available procedure in the literature was modified suitably and used for the synthesis of said complexes [6].

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doi:10.1016/j.jfluchem.2007.05.001

2. Results and discussion

The procedure adopted for the synthesis of MPcOF's yield pure complexes. The title complexes are dark green in color except for that of zinc, which is green with brown tinge. These complexes give clear solution in concentrated sulfuric acid and are sparingly soluble in DMSO, DMF and pyridine, and the solubility is in the order of $H_2SO_4 > DMSO > DMF > pyridine$. The results of elemental analysis for carbon, hydrogen and nitrogen are given in Table 1 and are in good agreement with the calculated values and are consistent with the suggested structure in Fig. 1. The reduction of nitro derivatives to the corresponding amino derivatives and the conversion of later into MPcOF's were almost quantitative with good yield.

2.1. IR spectra

The infrared spectra were recorded using KBr pellets and the results are presented in Table 2 and their spectra are given in Fig. 2. A broad absorption band at 3384–3379 cm^{-1} was observed for all the complexes and was assigned to the hydrogen bonding formed between the nitrogen atom of the phthalocyanine molecule and hydrogen atom of the moisture absorbed on KBr pellets during pelletization [12]. The peaks observed in the range of 1621–1548 and 1347–1352 cm^{-1} were assigned respectively to C=C aromatic stretching and C–N aromatic stretching vibrations. The sharp peaks in the range of 586–757 cm^{-1} were assigned to C–F stretching frequencies of the peripheral substitution on the phthalocyanine ring. The remaining peaks in the range of 1093–1098 and 1388–1403 cm^{-1} were attributed to various skeletal vibrations of phthalocyanine ring [13].

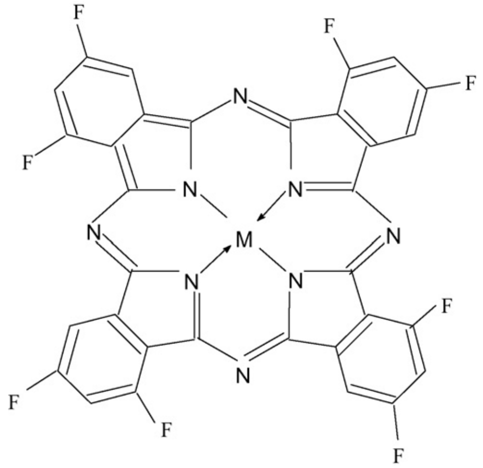


Fig. 1. The proposed structure of metal 1,3,8,10,15,17,22,24-octafluorophthalocyanines, MPcOF where M = Cu(II), Co(II), Ni(II) and Zn(II).

2.2. Electronic spectra

The electronic spectra of title complexes were recorded in the concentration range of $1.0–1.5 \times 10^{-4}$ M in 1:1 sulfuric acid and the data are summarized in Table 2. For all the complexes peaks were observed in the range of 243–326 nm are assigned for a B-band due to $a_{2u} \rightarrow e_g$ transitions. The peaks observed for Cu(II), Co(II) and Ni(II) complexes in the

Table 1
Elemental analysis and magnetic susceptibility, of 1,3,8,10,15,17,22,24-octafluorophthalocyanines of Cu(II), Co(II), Ni(II) and Zn(II)

Complex (yield, g) [color]	Empirical formulae (formula weight)	Field (kG)	Magnetic susceptibility, χ_m ($\times 10^{-6}$)	Magnetic moments μ_{eff} (BM)	Elemental analysis [found (calc.)]
CuPcOF (90%, 4.5) [dark green]	$C_{32}H_8N_8F_8Cu$ (719.47)	1.03	+2263.01	2.35	C: 54.08 (53.37)
		1.30	+2074.01	2.25	H: 1.47 (1.12)
		1.51	+1610.02	1.98	N: 15.70 (15.94)
		1.83	+1594.50	1.97	F: 21.12 (21.25)
		2.09	+1351.68	1.82	Cu: 8.48 (8.53)
		2.32	+1281.59	1.72	
CoPcOF (90%, 4.5) [dark green]	$C_{32}H_8N_8F_8Co$ (714.85)	1.03	+2348.29	2.39	C: 54.58 (53.72)
		1.30	+2154.41	2.29	H: 1.27 (1.12)
		1.51	+2044.59	2.24	N: 15.46 (15.66)
		1.83	+1910.67	2.16	F: 21.32 (21.20)
		2.09	+1744.38	2.06	Co: 8.68 (8.53)
		2.32	+1661.03	2.01	
NiPcOF (90%, 4.5) [dark green]	$C_{32}H_8N_8F_8Ni$ (714.62)	1.30	−521.02	–	C: 54.18 (53.73) H: 1.41 (1.12) N: 15.66 (15.67) F: 20.98 (21.02) Ni: 8.18 (8.21)
ZnPcOF (80%, 4.0) [green with brown tinge]	$C_{32}H_8N_8F_8Zn$ (721.30)	1.30	−1099.00	–	C: 53.58 (53.23) H: 1.23 (1.11) N: 15.68 (15.53) F: 21.63 (21.06) Zn: 9.13 (9.06)

Table 2
Spectral data of metal(II)-1,3,8,10,15,17,22,24-octafluorophthalocyanines of Cu(II), Co(II), Ni(II) and Zn(II)

Complex	UV–vis wave length, λ in nm (log ε)	IR spectral data (cm^{-1})	Powder XRD data, 2θ (°) (d in Å)	Relative intensity (%)
CuPcOF	326 (3.77)	757, 907, 1098, 1352, 1548, 1616, 1714, 2355, 3384	23.31 (3.75)	81.81
	473 (3.36)		26.01 (3.29)	99.17
	647 (3.14)		27.01 (3.24)	100.00
	735 (3.16)		27.92 (3.14)	90.49
			28.09 (3.12)	80.99
CoPcOF	243 (3.78)	752, 1093, 1347, 1388, 1543, 1621, 1698, 2345, 3384	17.65 (4.930)	94.70
	444 (3.25)		22.27 (3.92)	100.00
	715 (2.99)		23.25 (3.75)	96.03
			26.88 (3.25)	99.66
			41.30 (2.14)	92.05
			45.90 (1.94)	92.05
NiPcOF	260 (3.48)	741, 1093, 1347, 1390, 1543, 1616, 1703, 2360, 3379	16.14 (5.39)	58.11
	479 (3.09)		18.39 (4.74)	61.32
	620 (2.84)		23.28 (3.75	76.75
			25.51 (3.43)	82.92
			26.69 (3.28)	100.00
			43.33 (2.05)	55.40
ZnPcOF	254 (3.49)	586, 757, 1352, 1403, 1543, 1616, 1719, 2355, 3384	17.21 (5.05)	67.65
	553 (3.15)		20.67 (4.22)	75.53
	616 (3.00)		22.98 (3.80)	84.31
			26.44 (3.31)	100.00
			27.76 (3.15)	92.16
			28.75 (3.05)	74.51

range of 473–479 nm are found to be blue shifted compared to the corresponding parent phthalocyanines [14]. For Cu(II), Ni(II) and Zn(II) complexes peaks are observed in the range of 616–647 nm are attributed to the Q-band due to $a_{1u} \rightarrow e_g$ transitions. However, such peaks were not observed in the case of CoPcOF. For CoPcOF and CuPcOF sharp peaks were observed in the wavelength range 715–785 nm which is attributed to $\pi \rightarrow \pi^*$ transitions of the phthalocyanine ring.

2.3. Magnetic susceptibility

The magnetic susceptibility χ_m, and magnetic moments μ_{eff} values of square planar MPcOF's have been investigated in the solid state over a range of 1.03–2.32 kG and results are summarized in Table 1. The values reported are the average of three independent determinations. The magnetic susceptibility studies revealed that CuPcOF and CoPcOF are paramagnetic and NiPcOF and ZnPcOF are diamagnetic complexes. The measured magnetic moments for CuPcOF and CoPcOF are higher than that expected for that of one unpaired electron and at higher filed it approaches the spin only value (1.73 BM). The observed higher magnetic moments than spin only value is due to the orbital contribution to μ_{eff} which may arise as a result of mixing of ground state orbitals $(b_{2g})^2$, $(e_g)^4$ and $(a_{1g})^1$ with higher orbitally degenerate states $(b_{2g})^2$, $(e_g)^3$ and $(a_{1g})^2$. The orbital contribution is found to be higher at lower magnetic filed than that of higher one evidenced by higher μ_{eff} values at lower field strength and it is attributed to intermolecular magnetic interaction coupled with magnetic anisotropy of phthalocyanine π-electronic current as reported in the literature [15].

The crystallographic studies revealed that the metal phthalocyanines of Co, Ni, Cu and Zn have square planar structure with D_{4h} symmetry and are isomorphous (BNA & JK, Polyhedron). The molecular plane is approximately normal to *a*–*b*-axis. The molecular planes are inclined to *a*–*c*-axis at an angel 45°. Thus the complexes stacked in column with N-atom above and below on every metal atom (Fig. 3) and hence the nearest neighboring molecule along *b*-axis contributes a nitrogen atom at the interplanar distance 3.8 Å [16].

The overlapping of two neighboring molecules depends on the crystal modification. The XRD data reveals that the MPcOF's are in β-form. The metal(II) of one of the phthalocyanine overlap with N-atom of azamethine atom of the other metal phthalocyanine molecule.

2.4. Thermogravimetric studies

Thermogravimetric analytical data of the title complexes are recorded in air and in nitrogen atmosphere and the data are presented in Table 3. It is observed that in air the decomposition of the complexes occurs in two distinct steps and char residue is found to be in the range of 15–20% corresponding to their metal oxides. The initial weight loss of 1–2% was observed for all the complexes corresponding to the loss of free moisture. All the complexes shown a weight loss of 20–22% in the temperature range of 200–310 °C which corresponds to the loss of functional group fluoride present at the periphery of the macromolecule. The major weight loss of 70–75% was

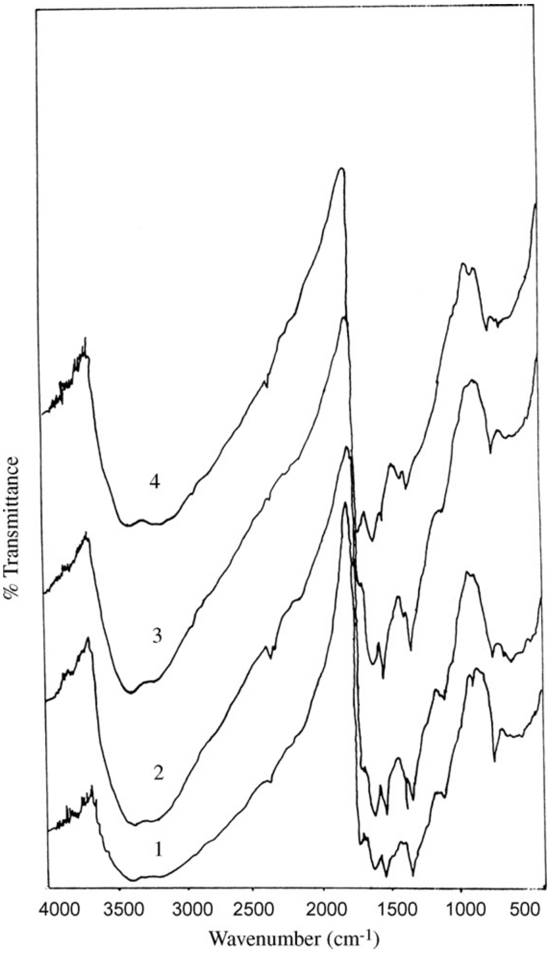


Fig. 2. IR absorption spectra of (1) CuPcOF, (2) CoPcOF, (3) NiPcOF and (4) ZnPcOF.

observed for all the complexes in the temperature range of 650–710 °C corresponding to the oxidative degradation of phthalocyanine moiety. The DTA data revealed that all degradation steps are exothermic in nature. However, in the nitrogen atmosphere even though weight loss occurs in two steps, but the title compounds did not degrade completely event at 800 °C and the final product leftover was found to be in the range of 36–40%.

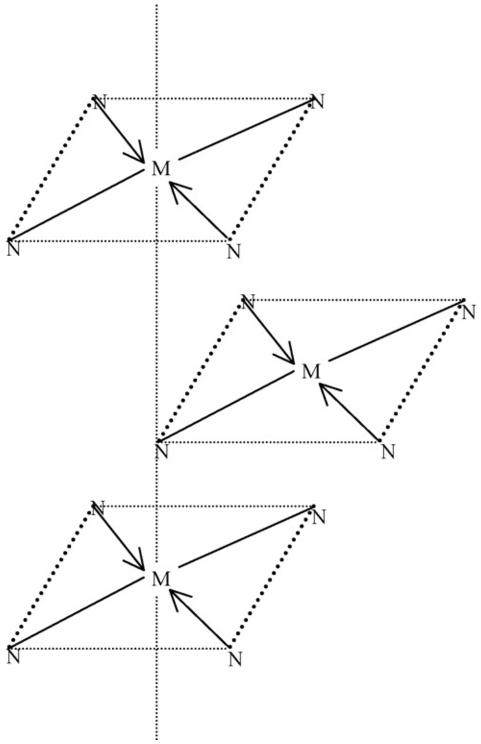


Fig. 3. Probable molecular stacking of metal phthalocyanines. M = Cu, Co, Ni and Zn, N = azamethine atom of phthalocyanine.

The observed thermal stabilities of MPcOF's in air was in the order of CuPcOF > CoPcOF > NiPcOF > ZnPcOF.

The kinetic and thermodynamic parameters of the title complexes have been evaluated by Broido's method [17] for the two stages of decomposition. The plots of ln(ln 1/y) versus 1/T (where y is the fraction of the complex undecomposed) were developed in air and nitrogen atmosphere for the decomposition segments corresponding to the loss of functional groups, fluorine and degradation of phthalocyanine moiety. The corresponding plots are shown in Figs. 4 and 5 (a for first stage in air and b for second stage in nitrogen atmosphere). From the plots, the activation energy (E_0) and frequency factor (ln A) were evaluated. The enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) have been computed using standard equations and are summarized in Table 4.

Table 3
TGA data of 1,3,8,10,15,17,22,24-octafluorophthalocyanines of Cu(II), Co(II), Ni(II) and Zn(II)

Compound	Temperature of decomposition (°C)	Mass loss		Probable fragment loss	Nature of DTA peaks
		% Found	% Calc.		
CuPcOF	200–310	0.4563 (0.3872)	0.4752 (0.1814)	8F groups	Exothermic
	650–710	1.7037 (1.4307)	1.7280 (0.9070)	Pc moiety	
CoPcOF	200–320	0.7493 (0.4278)	0.7753 (0.2012)	8F groups	Exothermic
	650–720	2.7979 (1.5973)	2.8192 (0.9648)	Pc moiety	
NiPcOF	200–305	0.5972 (0.6662)	0.5616 (0.4698)	8F groups	Exothermic
	650–710	2.2300 (2.4874)	2.1902 (1.5036)	Pc moiety	
ZnPcOF	200–308	0.7778 (0.3810)	0.7551 (0.2169)	8F groups	Exothermic
	650–720	2.9042 (1.4225)	2.9582 (0.9944)	Pc moiety	

Pc, phthalocyanine. The values in parentheses represent the data in nitrogen atmosphere.

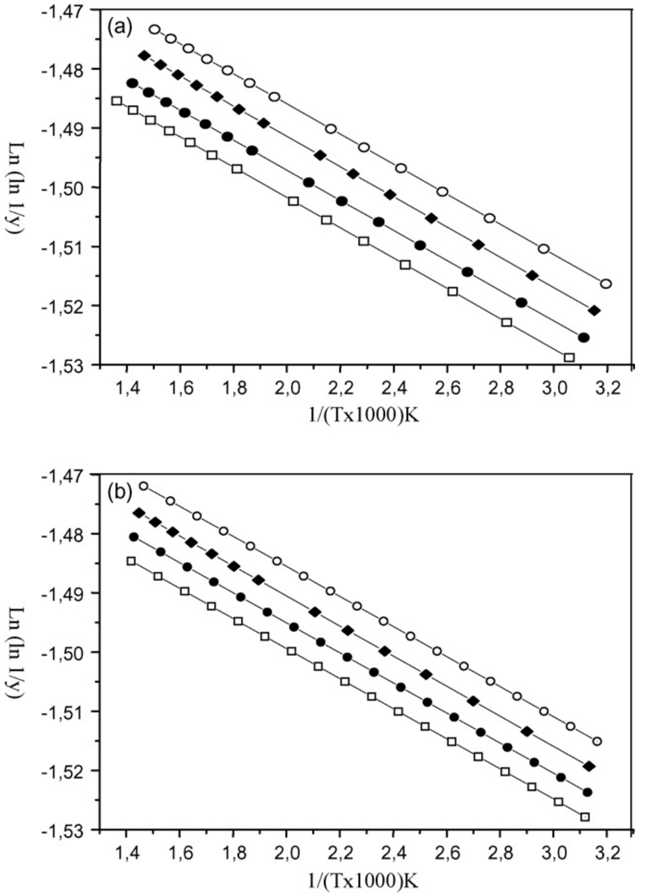


Fig. 4. Plots of ln(ln 1/*y*) vs. 1/(*T* × 1000) K for the first step decomposition of MPcOF's (a) in air and (b) in nitrogen atmosphere (◇) for CuPcOF, (●) for CoPcOF, (◆) for NiPcOF and (○) for ZnPcOF.

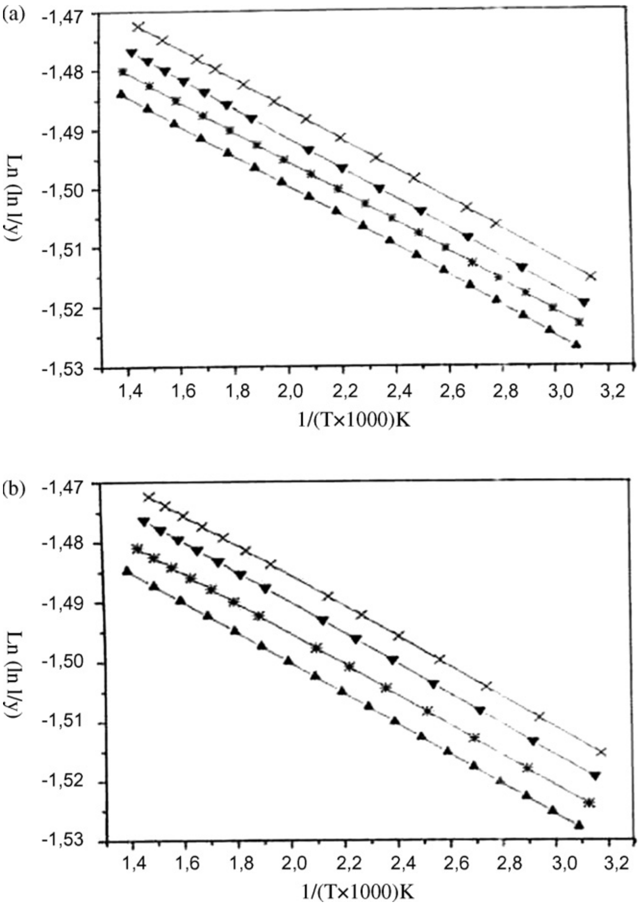


Fig. 5. Plots of ln(ln 1/*y*) vs. 1/(*T* × 1000) K for the second step decomposition of MPcOF's (a) in air and (b) in nitrogen atmosphere (▶) for CuPcOF, (✱) for CoPcOF, (◀) for NiPcOF and (×) for ZnPcOF.

The activation energies, E_0 for the loss of substitutents for all the complexes lies in the range of 0.47–0.68 K/(J mol). The exothermic behavior of the degradation of the substituted phthalocyanines is clearly indicated by the negative values of enthalpies.

The change in entropy (ΔS) are negative for all the complexes and varies from −106.48 to −177.36 J/K clearly indicates that the removal of functional group of the complexes are associated with negative values.

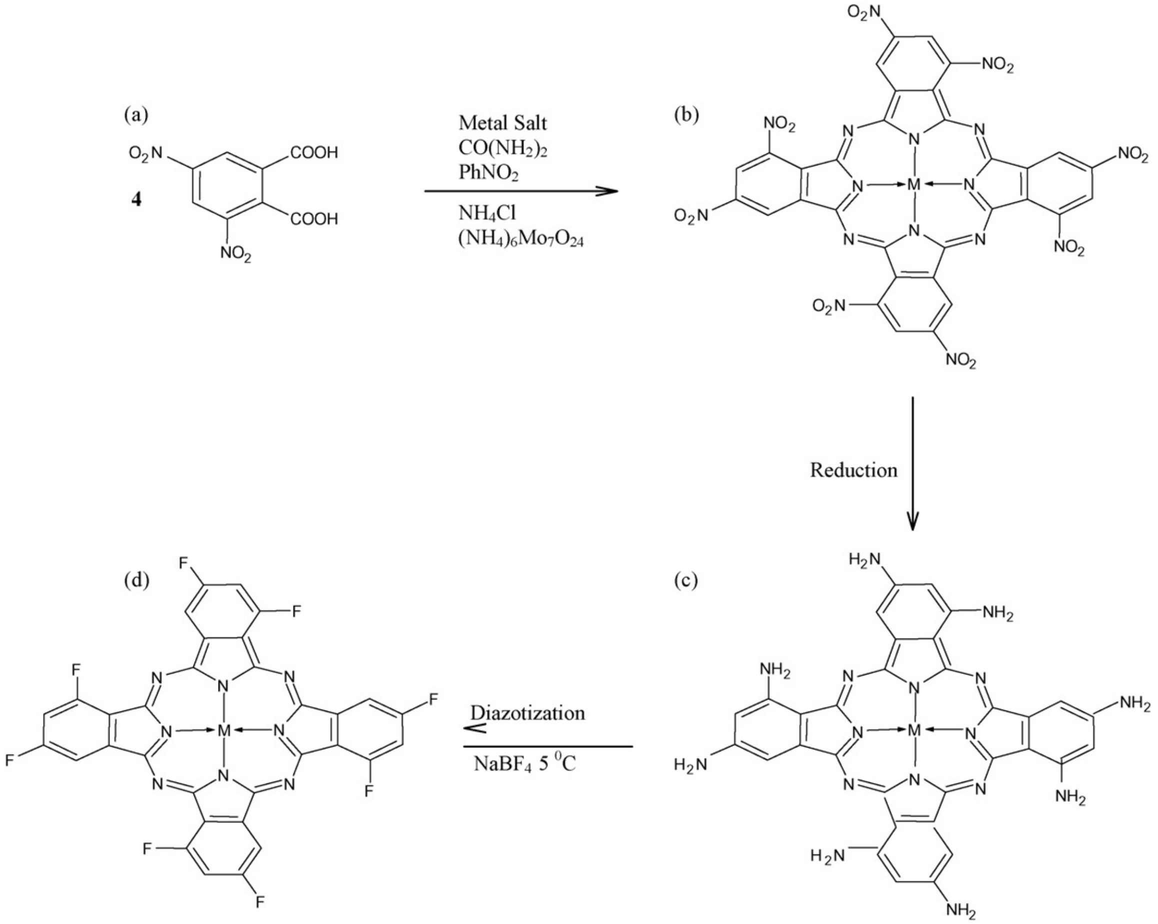
2.5. Powder XRD

The X-ray diffraction spectra of MPcOF's taken through a range of 2θ angles 6–70 °C showed identical peaks with very

Table 4
Kinetic and thermodynamic parameters of 1,3,8,10,15,17,22,24-octafluorophthalocyanines of Cu(II), Co(II), Ni(II) and Zn(II) in air and nitrogen atmosphere

Compound	Activation energy, E_0 (kJ/mol)	Frequency factor, ln *A*	ΔH (kJ/mol)	ΔS (J/K)	ΔG (kJ/mol)
CuPcOF					
I	0.4788 (0.6812)	1.95 (3.29)	−1.225 (−1.064)	−156.85 (−156.77)	32.15 (22.27)
II	11.92 (0.3925)	5.24 (2.57)	6.073 (−5.593)	−144.68 (−145.32)	102.72 104.62
CoPcOF					
I	0.5826 (0.7049)	6.09 (3.35)	−1.163 (−1.040)	−106.48 (−105.70)	22.36 (22.19)
II	11.9769 (5.2489)	7.937 (5.938)	5.990 (−0.6529)	−118.47 (−145.77)	85.30 (103.49)
NiPcOF					
I	0.6778 (0.6421)	3.310 (3.253)	−0.985 (1.020)	−156.89 (−145.27)	31.37 (28.03)
II	11.8126 (5.0956)	7.892 (5.892)	5.992 (0.724)	−148.20 (−150.23)	109.73 (104.43)
ZnPcOF					
I	0.6778 (0.6659)	2.964 (3.400)	−0.985 (0.996)	−177.36 (−177.67)	34.48 34.13
II	20.8282 (7.1415)	9.966 (6.573)	14.925 (1.238)	−22.965 (−138.43)	31.23 (99.52)

The values in parentheses represent the data in nitrogen atmosphere.



Scheme 1. Synthesis of metal(II)-1,3,8,10,15,17,22,24-octafluorophthalocyanine, (a) 3,5-dinitrophthalic acid, (b) MPcON, (c) MPcOA and (d) MPcOF.

poor crystallinity (Table 2). The observed patterns are very much similar to that of unsubstituted parent phthalocyanines except the broadening of the peaks in case of title complexes with diffused intensity. This broadening may be due to the presence of substitutents and which seems to play an important role in the stacking of the metal phthalocyanine derivatives. X-ray diffraction patterns are used only to explain the degree of crystallinity qualitatively.

3. Conclusion

The synthetic route adopted was very simple and give good yield. The blue shift of the complexes compared to the parent phthalocyanine is due the fluorine group at the peripheral substitution. The magnetic susceptibility studies clearly revealed the structural information of the complexes. The observed thermal stabilities of MPcOF's in air was in the order of CuPcOF > CoPcOF > NiPcOF > ZnPcOF.

4. Experimental

The pure 3,5-dinitrophthalic acid was prepared by the nitration of 2-methyl benzoic acid at −10 °C followed by oxidation of the same by using sodium dichromate in acid condition [6], and all other chemicals used were of analytical grade. The metal(II)-1,3,8,10,15,17,22,24-octanitropthalocyanines were prepared by the reported procedure [7]. These complexes are converted into the respective amino derivatives using the documented procedure [8]. The substituted amino complexes are converted into fluoro derivatives using the chemistry of Sandmeyers reaction with suitable modification [9] as per Scheme 1.

4.1. Preparation of copper(II)-1,3,8,10,15,17,22,24-octafluorophthalocanine

Copper(II)-1,3,8,10,15,17,22,24-octaaminophthalocanine (5 g) was taken in 50 mL of 1N H_2SO_4 and the temperature of the mixture was brought down to 5 °C. To this chilled solution, aqueous solution of sodium nitrite (6.2 g/10 mL, chilled) was added in small volumes at a time with constant stirring and maintaining the temperature below 10 °C to get copper(II)-1,3,8,10,15,17,22,24-octadiazoniumsulfate.

The chilled aqueous solution of sodium tetrafluoroborate (12.72 g/200 mL) was added slowly with constant stirring to the clear solution of copper(II)-1,3,8,10,15,17,22,24-octadiazoniumphthalocyanine hydrogen sulfate [$CuPcO(N_2^+HSO_4^-)$] maintained below 10 °C. After stirring the mixture for about 15–20 min, the solution was heated on a water bath until the evolution of nitrogen ceases. The green solid was separated by decantation and washed thrice alternatively with 1.0 M sodium hydroxide and 1.0 M hydrochloric acid and finally with distilled water. Copper(II)-1,3,8,10,15,17,22,24-octafluorophthalocanine was separated by centrifugation, dried at 100 °C for 30 min and finally in a vacuum descicator over anhydrous phosphorous pentaoxide. CoPcOF, NiPcOF and ZnPcOF were prepared similarly by using the respective octaaminophthalocyanines.

4.2. Methods

C, H and N analysis were performed at Punjab University, Regional Sophisticated Instrumentation Center, Chandighar, India. The magnetic susceptibility at room temperature (301 K) was carried out using Gouy magnetic balance consisting of NP-53 type electromagnets with a DC power supply unit and a digital semi-micro balance. Pascal constants were used to calculate the diamagnetic corrections [10]. The calibrant $Hg[Co(SCN)_4]$ was used. Shimadzu UV-Visible recording Spectrometer, UV-160A with 1 cm cell width was used for electronic absorption spectra. IR spectra were recorded using Nicolet MX-FT IR spectrometer. Phillips Analytical PW1710 X-ray diffractrometer was used to study the diffraction pattern. The spectra were recorded using Cu Kα as target material, voltage of 40 kV, a current of 20 mA, a time constant of 4, a channel width of 7 mm and chart speed of 10 mm/min. Perkin-Elmer Thermal analyzer was used for simultaneous record of TGA and DTA at the heating rate of 10 °C/min.

Acknowledgements

The authors are thankful to the chairman, department of Industrial chemistry for providing the basic laboratory facilities. One of the author (KRVR) thanks the UGC, India, for the award of FIP-Teacher Fellowship.

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