

Synthesis and Magnetic, Spectral and Thermal Studies on Metal 1,3,8,10,15,17,22,24-Octanitrophthalocyanines

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A simple and novel method for the preparation of 1,3,8,10,15,17,22,24-octanitrophthalocyanine derivatives, MPcON's (M = Fe (III)Cl, Zn(II), Co(II), Cu(II) and Ni(II)), was developed. The dark green complexes were characterized by elemental analysis, electronic spectra, IR spectra, thermogravimetry, differential thermal analysis, powder X-ray diffraction and magnetic susceptibility.

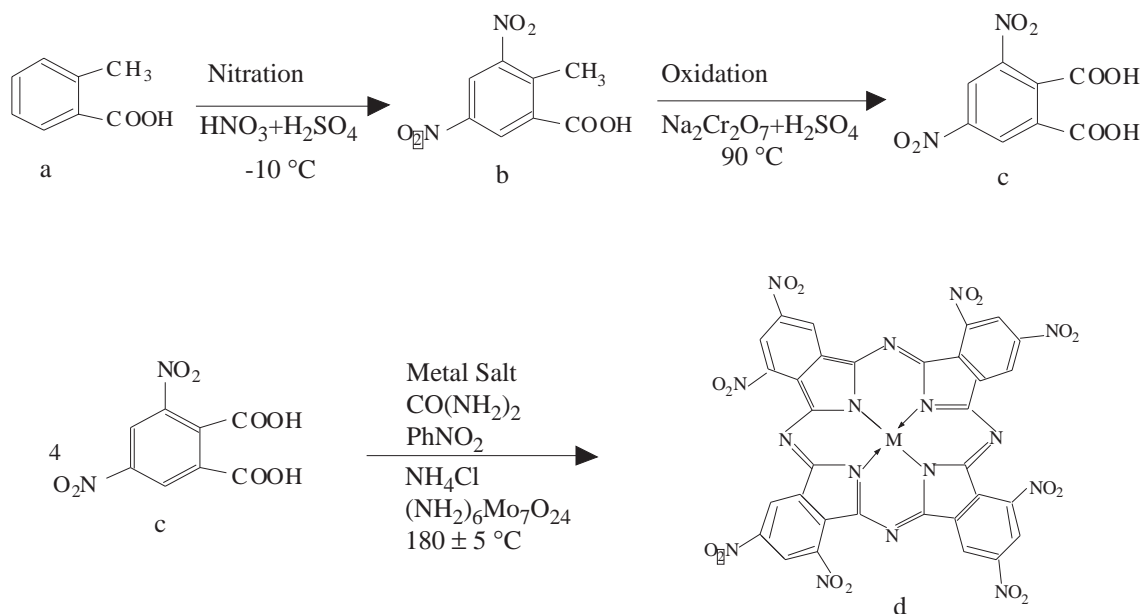
Introduction

The earlier interest in metal phthalocyanines was mainly because of their importance as dyes and pigments¹⁻³. Recently, intensive research has focussed on producing phthalocyanines for catalysts⁴, photosensitizers¹, photoconductivity¹⁻⁴, thermally stable polymers⁵⁻¹⁰ and for photodynamic therapy¹¹. Versatile properties like electrical conductivity, thermal stability, catalytic properties, photoconductivity and chemical resistance of these complexes are influenced by the nature of the metal, and peripheral substitution in the phthalocyanine ring. The present work describes the synthesis and characterization of 1,3,8,10,15,17,22,24-octanitrophthalocyanine derivatives of Zn (II), Fe (III)Cl, Co(II), Ni(II) and Cu(II). The method outlined here is taken from the methods described for the synthesis of different types of phthalocyanine derivatives¹². For the sake of comparison, CuPcON, CoPcON and NiPcON were synthesized and characterized by adopting the reported procedure.

Experimental

Metallo 1,3,8,10,15,17,22,24-octanitrophthalocyanines (MPcON's) were synthesized by the following scheme.

The detailed procedure for the synthesis of Zinc(II)-1,3,8,10,15,17,22,24-octanitrophthalocyanine is outlined as follows.



Scheme. Synthesis of Metal 1,3,8,10,15,17,22,24 octanitrophthalocyanines, MPcONs **a.** *o*-Toluic Acid, **b.** 3,5-dinitrotoluic acid, **c.** 3,5-dinitrophthalic acid, **d.** Metal 1,3,8,10,15,17,22,24-octanitrophthalocyanines.

Synthesis of Zinc (II)-1,3,8,10,15,17,22,24-octanitrophthalocyanine

A finely ground mixture of zinc sulphate heptahydrate (3.2 g, 0.01 mol), 3,5-dinitrophthalic acid (10 g, 0.04 mol), ammonium chloride (1.2 g, 0.02 mol), ammonium molybdate (catalytic quantity) and urea (15 g, 0.2 mol) was placed in a 500 mL three-necked flask containing nitrobenzene (15 g, 0.12 mol) as solvent. The mixture was maintained at a temperature of $180 \pm 2^\circ\text{C}$ for 30-45 min. The colour of the compound gradually deepened to yield a dark brown solid with a green tinge. The product was well ground and washed with MeOH until free from PhNO_2 and then treated with 1M HCl (100 mL) saturated with NaCl, boiled for 5 min, cooled to room temperature and centrifuged. The residue was treated with 1M NaOH (100 mL) and NaCl (25 g), and then heated to 90°C until the evolution of ammonia ceased. The solid product was again treated with HCl and NaOH alternately three more times. The resulting Zn (II)-1,3,8,10,15,17,22,24-octanitrophthalocyanine was washed with water until the residue was free from chloride ions. The dark green product was dried under vacuum in the presence of P_2O_5 . The yield was 55-65%. Similarly, CuPcON, CoPcON, NiPcON and FePcONCl were also prepared by the above method with suitable modifications.

C, H and N analyses were carried out by the Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh. The metal content was determined by incinerating them to the oxides. Magnetic susceptibility studies were carried out at room temperature (301 K) using a Gouy magnetic balance consisting of NP-53 type electromagnets with a DC power supply unit and a semi-microbalance. Pascal's constants were used to calculate the diamagnetic corrections¹³.

A Hg $[\text{Co}(\text{SCN})_4]$ complex was used as a calibrant. A Shimadzu UV-Visible recording spectrophotometer, UV-160A, with 1 cm-width cell was used for electronic absorption spectral studies. IR spectra were recorded using a Nicolet MX-FT IR spectrometer with KBr pellets in the range $4000\text{-}500\text{ cm}^{-1}$. A TGA/SDTA851e/SF1100/MTI/057 thermal analyser was used for the thermogravimetric studies with a heating rate of $10^\circ\text{C}/\text{min}$. A Philips analytical PW1710 X-ray diffractometer was used to study the X-ray diffraction pattern of the complexes. The spectra were recorded using $\text{Cu K}\alpha$ under the following conditions.

Voltage	Current	Time Constant	Channel Width	Chart Speed
40 kV	20 mA	4	7 mm	10 mm/min

Results and Discussion

The procedure used for the preparation of MPcON's yielded complexes in the range 55-65% and was higher than the yields of earlier reported methods¹⁴. Also the above complexes were synthesized by using microwave irradiation in the absence of solvent under suitable conditions. The yields of the complexes ranged from 65 to 70% and were of a dark bluish-green colour. These complexes are insoluble in water and most organic solvents like benzene, carbon tetrachloride, ether and alcohol, but soluble in DMSO, DMF and Pyridine. The results of elemental analysis for carbon, hydrogen and nitrogen are in agreement with the calculated values and are consistent with the proposed structure.

Electronic spectra

The electronic spectra of MPcON's in the concentration range $1.1-1.2 \times 10^{-4}$ M were recorded in DMSO and the results are summarized in Table 2. For all the MPcON's a peak was observed in the range 680-695 nm, which is attributed to a Q-band, $a_{1u} \rightarrow e_g$ transition, and 281-318 nm, which was a B-band, assigned to $a_{2u} \rightarrow e_g$ transition¹⁵. However, the absorption peaks for the corresponding unsubstituted metal phthalocyanines were in the ranges 327-336 nm (B-band) and 663-683 nm (Q-band)¹⁵. The Q-band in MPcON was observed to be red shifted. This shift may be due to the decrease in energy between various $\pi \rightarrow \pi^*$ transitions of the phthalocyanine ring as a function of the electron withdrawing nature of NO₂ groups on the periphery. Further, for CuPcON, CoPcON and NiPcON complexes, peaks were observed in the range 450-468 nm and for FePcONCl and ZnPcON shoulders were observed, which may account for the aggregation of the MPcON's in the solvent¹⁶. A band was observed for all the MPcON's in the range 214-216 nm and may account for the C-band of phthalocyanine molecules^{17,18}.

IR spectra

The IR spectral data of the MPcON's were recorded and are given in Figure 1 and the results are summarized in Table 2. A sharp peak was observed for all the complexes in the range 3426-3447 cm^{-1} , which may be assigned to the presence of hydrogen bonding between the oxygen or nitrogen atom of the nitro group and the hydrogen atom of the moisture absorbed on the KBr pellets. Sharp peaks at 1616-1641 cm^{-1} and 1476-1538 cm^{-1} may be assigned to the plane bending vibration of the NO₂ group. The sharp peak at 1347-1357 cm^{-1} and 1269-1274 cm^{-1} can be assigned to C - N aromatic stretching. All the remaining bands at 472, 560, 612, 669 and 793 cm^{-1} may be assigned to vibrations of the phthalocyanine ring¹⁷.

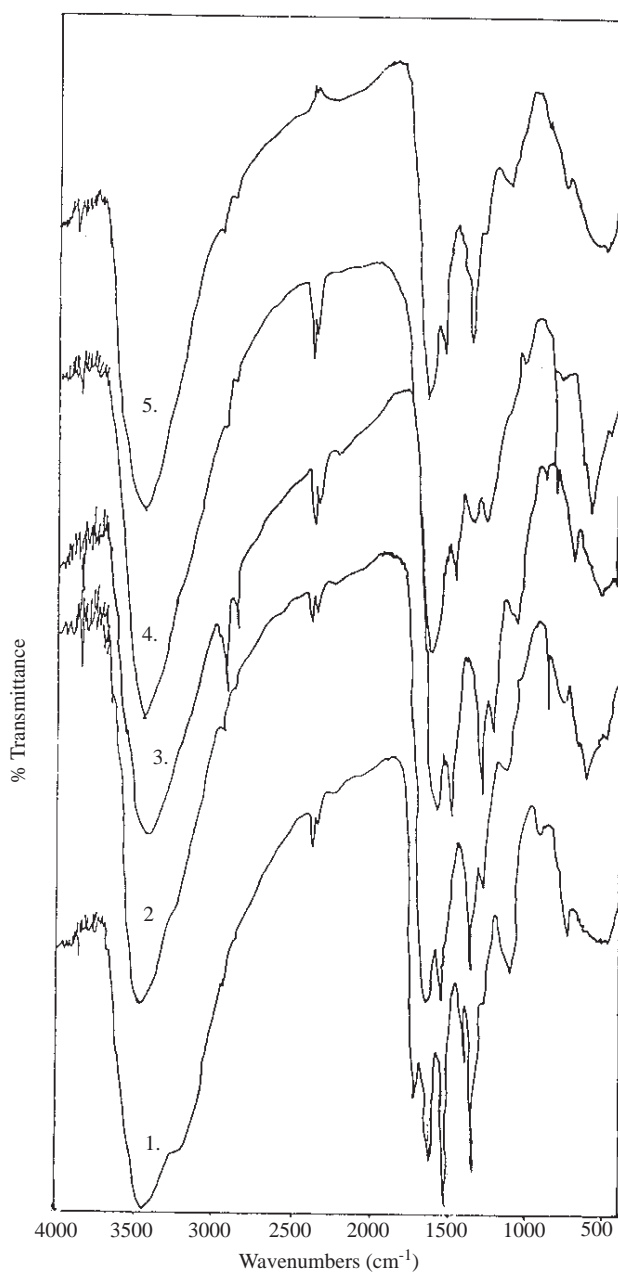


Figure 1. IR absorption spectra of **1.** CuPcON, **2.** NiPcON, **3.** ZnPcON, **4.** FePcONCl and **5.** CoPcON.

Magnetic Susceptibility

The magnetic susceptibility measurements for MPcON's were carried out in solid state at various field strengths and the results are summarized in Table 1. The measured magnetic properties of CuPcON, CoPcON and NiPcON are in agreement with reported data¹⁵. The results show that FePcONCl is paramagnetic and ZnPcON is diamagnetic. The measured values reveal that in all MPcON's the observed values for magnetic moments were much higher than the spin only values, which were higher than those for the corresponding unsubstituted metal phthalocyanines. The higher value of μ_{eff} indicates the presence of orbital contributions, which arise because of the mixing of ground state orbitals with higher orbitals of

degenerate states. The observed variations of magnetic moments with field strength for all complexes are in agreement with the trend observed for other phthalocyanine derivatives and may be due to an intermolecular cooperative effect^{12,14,17}.

Table 1. Elemental analysis and magnetic susceptibility data of - 1,3,8,10,15,17,22,24- octanitrophthalocyanines of Cu, Co, Ni, Zn and Fe

Complex	Emperical Formulae (Formula weight)	Field strength K Gauss	Magnetic susceptibility $\chi_m \times 10^{-6}$ cgs units	Magnetic moments μ_{eff} (B.M)	Elemental analysis found (Cal)
CuPcON	C ₃₂ H ₈ N ₁₆ O ₁₆ Cu (935.50)	1.27	+3750	3.06	C, 40.23, (41.05)
		1.71	+3437	2.88	H, 0.84, (0.86)
		2.58	+3332	2.84	N, 23.70, (23.94)
		3.44	+2569	2.49	Cu, 6.65, (6.70)
		4.27	+2458	2.44	
		4.68	+2420	2.42	
CoPcON	C ₃₂ H ₈ N ₁₆ O ₁₆ Co (930.93)	1.27	+4448	3.28	C, 40.50, (41.27)
		1.71	+4448	3.28	H, 0.85, (0.87)
		2.58	+3964	3.10	N, 23.97, (24.06)
		3.44	+2756	2.58	Co, 6.26, (6.32)
		4.27	+2031	2.22	
		4.68	+1789	2.08	
FePcONCl	C ₃₂ H ₈ N ₁₆ O ₁₆ ClFe (963.35)	1.27	+4801	3.41	C, 39.86, (40.38)
		1.71	+4358	3.25	H, 0.83, (0.86)
		2.58	+3489	2.91	N, 23.25, (24.04)
		3.44	+2964	2.68	Fe, 6.23, (6.03)
		4.27	+2440	2.43	Cl, 3.85, (3.75)
		4.68	+1915	2.15	
ZnPcON	C ₃₂ H ₈ N ₁₆ O ₁₆ Zn (937.38)	3.44	-980	—	C, 40.45, (40.96) H, 0.91, (0.85) N, 24.0, (23.89) Zn, 6.86, (6.97)
NiPcON	C ₃₂ H ₈ N ₁₆ O ₁₆ Ni (930.70)	3.44	-1775		C, 40.50, (41.27) H, 0.93, (0.85) N, 23.90, (24.06) Ni, 6.18, (6.30)

The higher μ_{eff} values observed for the MPcON's at lower magnetic field may be due to an intermolecular magnetic interaction coupled with the strong π -electron current of the phthalocyanine molecule. Crystallographic data¹⁷ has shown that each phthalocyanine molecule stacked next to the neighbouring molecule along the b-axis contributes either a N-atom at a distance of 3.38 Å one above and one below the central metal atom as shown in Figure 2(a), or may be placed one above the other with the separation of the two molecules at a distance of 3.38 Å as shown in Figure 2(b). This minimum interplanar separation seems to provide a pathway for spin-spin coupling between adjacent metal atoms either directly or super exchange through the N-atom of the molecule. The extent of exchange interaction depends primarily on the

angle of inclination of the plane of the molecule, type of metal ions and metal-metal separation. The exchange interaction coupled with orbital contributions seems to be the cause of the observed higher magnetic moment values for MPcON's at lower magnetic fields. At higher magnetic fields, the molecule suffers tumbling, resulting in a decrease in the intermolecular distance, which in turn favours effective intermolecular interaction.

Table 2. Spectral data of 1,3,8,10,15,17,22,24-octanitrophthalocyanines of Cu, Co, Ni, Zn and Fe

Complex	UV-visible Absorption λ nm (log ϵ)	IR Spectral data cm^{-1}	Powder XRD data 2θ angle (d Å)	Relative intensity %
CuPcON	217 (4.04)	3447,1636,1543,1352	31.78 (2.81)	100.00
	304 (4.40)	1114,917,752.	36.81 (2.44)	78.28
	470 (4.14)		44.70 (2.03)	64.40
	682 (4.05)			
CoPcON	216 (3.96)	3441,1626,1528,1347	31.77 (2.81)	100.00
	281 (4.26)	1264,1109,747.	36.74 (2.44)	42.93
	450 (3.79)		44.66 (2.02)	35.04
	680 (3.64)			
FePcONCl	216 (4.24)	3440,1616,1476,1357,1274,	31.77, (2.81)	100.00
	318 (4.10)	855, 793, 669, 612, 472	33.94, (2.64)	59.98
	460 (4.04)		45.49, (1.99)	56.73
	695 (4.12)			
ZnPcON	214 (4.20)	3430,1641,1631,1535,1347,	31.75, (2.81)	100.00
	316 (4.11)	1269, 669, 560	33.89, (2.64)	54.95
	468 (4.04)		45.52, (1.99)	49.38
	680 (4.11)			
NiPcON	214 (4.12)	3426,1616,1533,1341,1269,	31.82 (2.81)	100.00
	257 (4.48)	1119,850,747,602.	33.89 (2.63)	40.00
	318 (4.41)		45.55 (1.99)	57.78
	468 (4.20)			
	690 (4.03)			

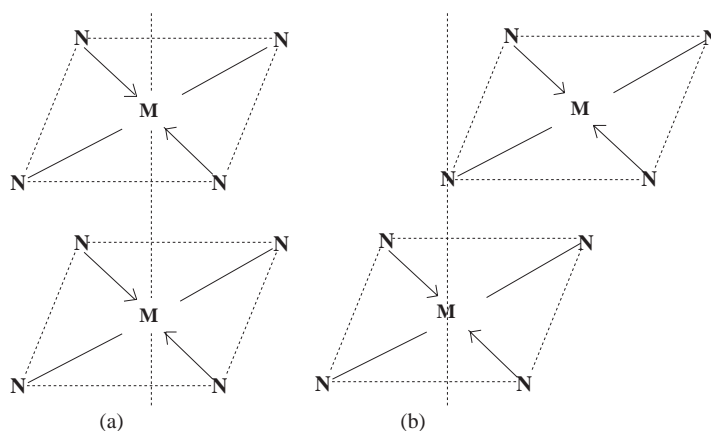


Figure 2. Probable molecular stacking of metal phthalocyanine for (a) direct and (b) super exchange intermolecular interactions. M = Cu, Co, Ni, Zn and Fe, N = Central nitrogen atoms of the phthalocyanine structure.

Powder XRD

The X-ray diffraction spectra of MPcON's taken through a range of 2θ angles $6-70^\circ$ showed identical peaks. Two peaks were observed: one sharp at a lower angle with maximum intensity and the other at a higher angle with higher intensity. The interplanar spacings on these angles gave the following values: FePcONCl, 2.81, 31.77 Å; ZnPcON 2.81, 31.75 Å; CuPcON 2.81, 31.78 Å; CoPcON, 2.81, 31.77 Å; and NiPcON 2.81, 31.82 Å clearly indicating the crystalline nature of the complexes.

Thermogravimetric Studies

All MPcON's were studied by thermogravimetric analysis in static air. Thermograms of MPcON's revealed that a weight loss of 2.3-3.0% was observed for all the complexes, corresponding to the loss of free moisture. All complexes except FePcONCl degrade in two distinct steps and the results are summarized in Table 3. CuPcON, CoPcON, NiPcON and ZnPcON displayed weight loss in the range $250-372^\circ\text{C}$, which corresponds to the loss of NO_2 functional groups present in the complexes. In the case of FePcONCl, even though there was a weight loss, no sharp weight loss was observed. The major weight loss was observed for all the complexes in the temperature range $425-549^\circ\text{C}$ corresponding to oxidative degradation of phthalocyanine moiety. DTA results revealed that all degradation steps are exothermic in nature. The final undecomposed products were found to be corresponding metal oxides.

Table 3. TGA and DTA data of 1,3,8,10,15,17,22,24-octanitrophthalocyanines of Cu, Co, Ni, Zn and Fe in air.

Name	Temp. of decomposition ($^\circ\text{C}$)	Mass loss % Found	Probable % Calcd.	Nature of fragments lost	DTA peak
CuPcON	278-372	39.1	37.1	$-\text{NO}_2$ groups	Exothermic
	465-577	53.8	56.4	Pc* moiety	
CoPcON	250-350	39.5	35.8	$-\text{NO}_2$ groups	Exothermic
	511-549	30.7	33.1	Pc moiety	
ZnPcON	250-340	39.2	38.0	$-\text{NO}_2$ group	Exothermic
	425-511	53.6	57.3	Pc moiety	
FePcONCl	— — —	—	—		
	501-560	54.4	57.0	Pc moiety	Exothermic
NiPcON	269-380	39.5	38.0	$-\text{NO}_2$ group	Exothermic
	462-537	54.0	57.7	Pc moiety	

Pc = Phthalocyanine

Conclusion

The magnetic susceptibility studies on the complexes showed that Co(II), Cu(II) and Fe(III)Cl complexes are paramagnetic and exhibited the variation of magnetic moment as a function of the magnetic field because of the intermolecular co-operative effect. The measured magnetic moment of complexes was higher than the spin only values due to orbital contributions, and these values were higher than those for the corresponding parent phthalocyanines. X-ray diffraction studies indicated the crystalline behaviour of the complexes. Thermal studies revealed the thermal stability of MPcON in air are in the order FePcONCl > CuPcON > NiPcON > ZnPcON > CoPcON. Electronic spectral studies showed the Q-band of MPcON's is redshifted compared to the corresponding parent phthalocyanine because of the decrease in energy between $\pi \rightarrow \pi^*$

transition of the phthalocyanine ring and the decrease is due to the presence of electron withdrawing NO₂ groups on the ring.

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