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

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Abstract

The present paper describes the synthesis and characterization of metal (II) 1,3,8,10,15,17,22,24-octachlorophthalocyanines (MPOCls) of copper (CuPOCl), cobalt (CoPOCl), nickel (NiPOCl) and zinc (ZnPOCl) by using modified Sandmayer's method. The dark green coloured octachloro substituted phthalocyanine derivatives are characterized by various physico-chemical techniques like elemental analysis, magnetic susceptibility, electronic, IR, thermal and powder X-ray diffraction to check the thermal stability, structural integrity and purity. The variation of magnetic moment as a function of field strength indicated the presence of intermolecular co-operative interaction.

Keywords: Phthalocyanines; Chiorooctasubstituted; Electronic; Magnetic; Thermal

1. Introduction

Phthalocyanines are man-made analogues of nature's pigments of life, the porphyrins, such as chlorophyll and hemoglobin. Since their discovery in 1907, phthalocyanines have become second only to the ubiquitous azo colorants in terms of commercial importance. The major commercial impact of phthalocyanines is based on three factors; the first is their beautiful bright blue to green colors and high tinctonal strength; the second is their remarkable thermal and chemical stability, e.g. copper phthalocyanine sublimes unchanged even at 580 °C and dissolves in cold concentrated sulfuric acid without decomposition. The third factor is their excellent fastness to light. This combination of properties is extremely difficult, if not impossible, to achieve in other colorants. By comparison, the natural dyes such as chlorophyll and haemin are highly sensitive and easily destroyed by light and mild chemical reagents [1]. Currently intensive research work is aiming at the production of useful phthalocyanines as sensitizers in PDT, catalysts in fuel cells, sensors, display devices, information storage systems [2], semi-

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conductors [3] and differential staining agents [4–6], toners in colour photocopiers and laser printers and hexadeca flurocopperphthalocyanines as the leading electron transport materials for organic semiconductors [1]. The literature survey revealed the methods for the synthesis of hexadecachioro, hexadecabromo, hexadecaiodo metal phthalocyanines and 1,4,8,11,15,18,22,25-octamethoxy and 2,3,9,10,16,17,23,24-octachlorophthalocyanines and those pigments were mainly used for commercial purposes [1]. Reports are available on the synthesis and structural investigations on symmetrically substituted 2,9,16,23 and 1,8,15,22-tetrachloro metal phthalocyanines [7,8]. Though synthetic procedures for 1,3,8,10,15,17,22,24-octanitro, octaamino and octobromophthalocyanines are documented in the literature [9–11], except a method reported by a Russian group of workers [12] no other reports are available on the synthesis and structural investigations on symmetrically octasubstituted metal (II)1,3,8,10,15,17,22,24-chlorophthalocyanines. The halogen substituents, especially chlorine and bromine, stabilize the α-form crystal structure but causes bathochromic shift, so that the halogenated pigments are greenish blues or greens, depending upon the degree of substitution [1]. Keeping the above facts in mind, a simple and economical method has been developed for the synthesis of the title complexes.

The present paper discusses the synthesis and structural studies on symmetrically substituted metal (II)1,3,8,10,15,17,22,24-octachlorophthalocyanines. The octanitro phthalocyanines were synthesized by using the available procedure [9] and were converted into respective amino derivatives through reduction [10]. The available procedure in the literature was suitably modified and is used for the synthesis of octachloro substituted metal (II) phthalocyanines [11].

2. Experimental

The procedure for the synthesis of metal (II) 1,3,8,10,15,17,22,24-octaaminophthalocyanines was reported elsewhere [10]. The amino substituted complexes are subjected to diazotisation in the presence of copper (I) chloride to produce title complexes by adapting Sandmeyrs reaction with suitable modifications [13]. The route followed for the synthesis of MPOCl′s is given in Scheme 1. All other chemicals used were of analytical grade.

2.1. Preparation of copper (II) 1,3,8,10,15,17,22,24-octachioro phthalocyanine

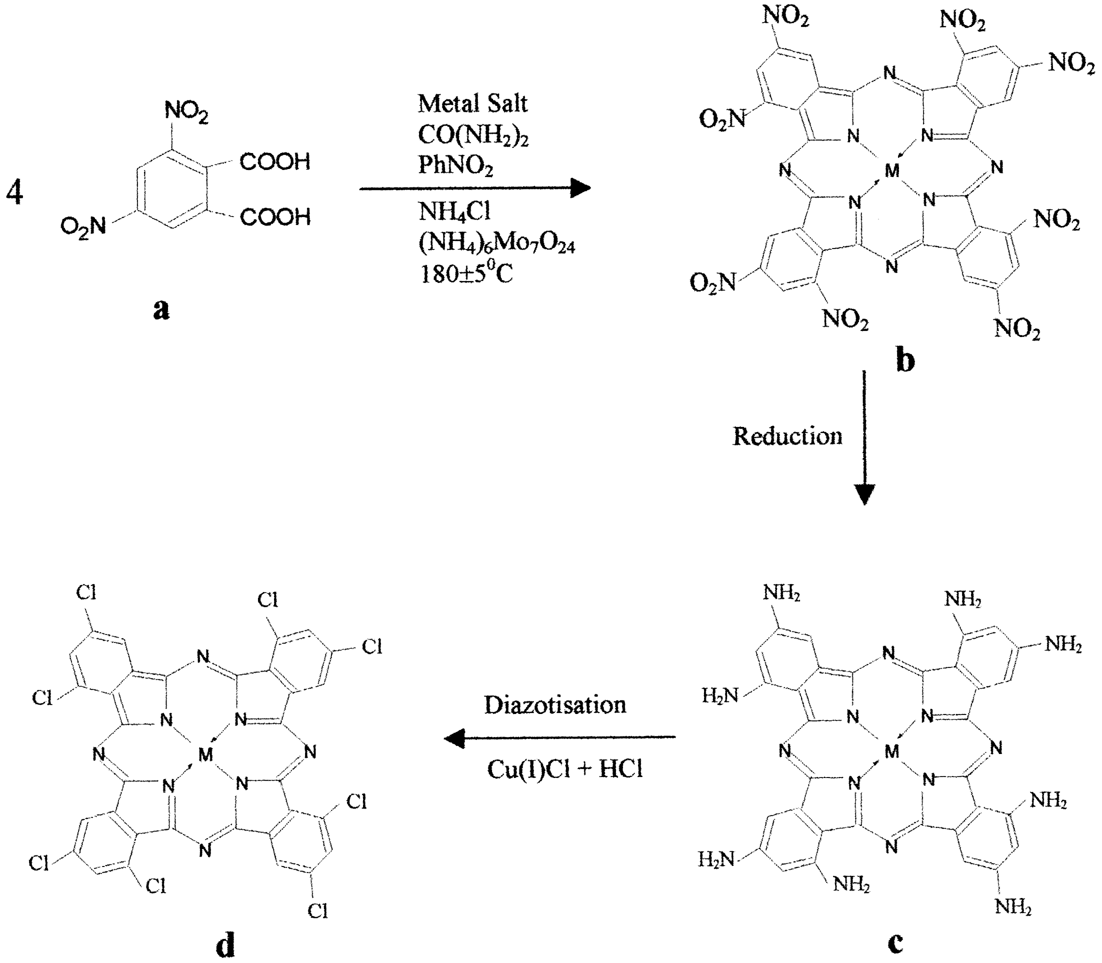
Five grams of copper (II) 1,3,8,10,15,17,22,24-octaaminophthalocyanine was diazotised in hydrochloric acid medium in the presence of stochiometric quantity of sodium nitrite to get octadiazonium salt of copper (II) phthalocyanine, $CuPON_2^+ Cl^-$, The mixture was maintained at a temperature below 5 °C using crushed ice.

Copper sulphate pentahydrate (26.42 g) and sodium chloride (6.20 g) were dissolved in 50 ml of water. Sodium bisulphite (5.12 g in 30 ml) was added slowly with constant stirring and then the contents allowed to attain the room temperature. The precipitate was washed thrice by decantation with water containing a little sulphurous acid. The moist colorless copper (I) chloride was dissolved in 20 ml of concentrated hydrochloric acid. The chilled solution of copper (II) 1,3,8,10,15,17,22,24-octadiazonium phthalocyanine chloride was added slowly to the chilled copper (I) chloride solution with constant stirring. The mixture became thick due to the separation of an additional product which formed between diazonium salt and copper (I) chloride ($CuPON_2^+ Cl^-$, CuCl). The mixture was then allowed to attain room temperature with occasional shaking. it was then warmed on a water bath at about 60 °C for the complete decomposition of the double salt, till the evolution of nitrogen ceased.

Clear solution was removed by decantation and residue was washed with water. The green product was centrifuged and washed with 1.0 M sodium hydroxide and 1.0 M hydrochloric acid thrice alternatively and finally with distilled water. The solid copper (II) 1,3,8,10,15,17,22,24-octachloro phthalocyanine was then dried in an oven at 50 °C for an hour followed by drying with anhydrous phosphorous pentoxide in a vacuum desiccator, yield 90%.

Octachloro phthalocyanine derivatives of Co (II), Ni (II) and Zn (II) were prepared by the above method by using the respective metal octaamino phthalocyamnes.

The Regional Sophisticated Instrumentation Center, Punjab University, Chandighar, India made the C, H, and N elemental analysis. The magnetic susceptibility studies were made at room temperature (301 K) using 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 corrections. A Hg [Co (SCN)$_4$] complex. was used as calibrant. [14] Shimadzu UV-Visible recording spectrophotometer, UV-160A with a 1 cm width cell was used for electronic absorption spectral studies. IR spectra were recorded using Nicolet MX-FT IR spectrometer. Philips analytical PW 1710 X-ray diffractometer was used to study the diffraction pattern of the complexes. The spectra were recorded using Cu K_α at a voltage of 40 KV, a current of 20 mA, a time constant of 4, a channel width of 7 mm and a chart speed of 10 mm/mm. TGA/SDTA 85e/SF I 100/MTI/057 thermal analyzer was used for thermogravimatric studies at a heating rate of 10 °C min^{-1}.



Scheme 1. Synthesis of metal-1,3,8,10,15,17,22,24-octachlorophthalocyanine: **a**. 3,5-dinitophthalic acid, **b**. MPON, **c**. MPOA and **d**. MPOCI.

3. Results and discussion

The procedure used for the synthesis of MPOCls resulted in pure compounds and have a dark green colour for Cu (II), Co (II), Ni (II) and green with a brown tinge for Zn (II). The metal phthalocyanine complexes are thermally stable and their resistance towards concentrated sulfuric acid was attributed to the atomic radii of the metal ions in the close range of 1.35Å[14]. These complexes give a clear solution with concentrated sulfuric acid and are fairly solible in DMSO, DMF and pyridine but insoluble in water and in most other common organic solvents like alcohol, ether, carbon tetrachioride and benzene. The results of elemental analysis for carbon, hydrogen, nitrogen and metal are in good agreement with the calculated values and are consistent with the proposed structure (Fig. 1).

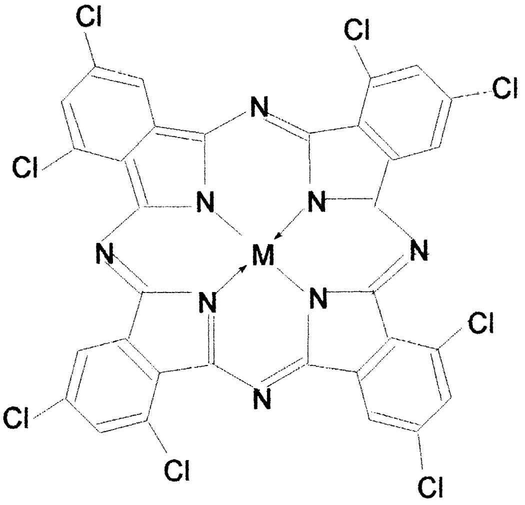


Fig. 1. The proposed structure of metal 1,3,8,10,15,17,22,24-octachlorophthalocyanines, MPOCl where M Cu,Co, Ni and Zn.

4. IR spectra

IR spectral data of title complexes were recorded in KBr pellets and the results are tabulated in Table 2. and the graphs are given in Fig. 3. A broad peak at 3400–3415 cm^{-1} was observed for all MPOCls and is attributed to the hydrogen bonding that may be formed between the nitrogen atom of the phthalocyanine macromolecule and H

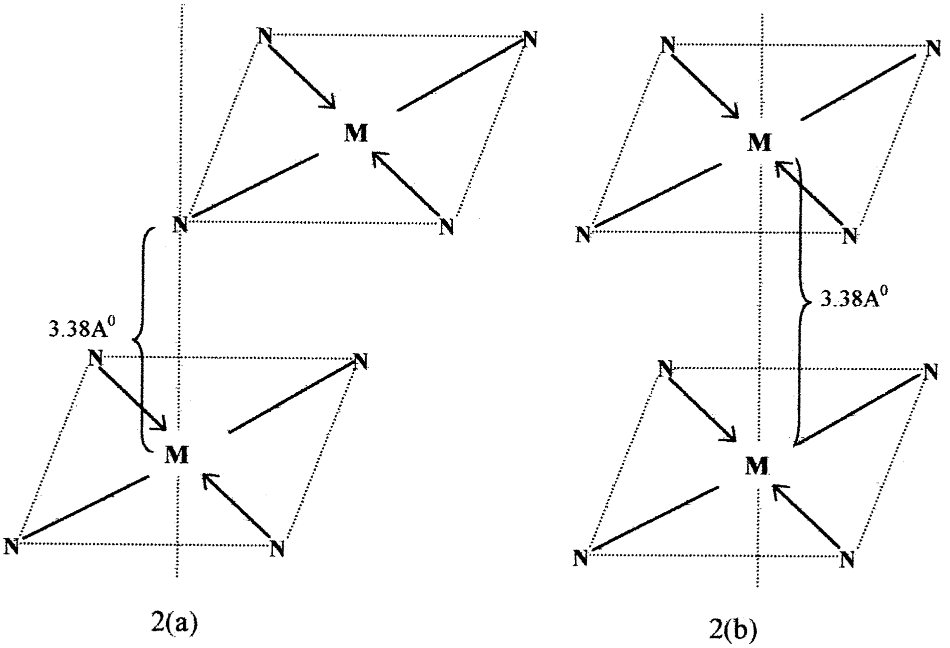


Fig. 2. Probable molecular stacking of metal phthalocyanines: M = Cu and Co, N = central nitrogen atoms of the phthalocyanine structure.

atoms of the moisture absorbed on the KBr pellets [15]. The sharp peaks observed at 1610–1616 cm^{-1} were attributed to C=C, C=N and ring stretching (skeletal band) [16]. The peaks at 1342–1388 cm^{-1} are due to C–H symmetric bending. The absorption bands that appeared around 749–772 cm^{-1} were assigned to C–Cl stretching frequency of the peripheral substitution on the ring. All other remaining peaks that appeared around 876–881 cm^{-1}, 1072–1088 cm^{-1} and 1300–1316 cm^{-1} are attributed to the various skeletal vibrations of phthalocyanine ring [17].

5. Magnetic susceptibility

The magnetic susceptibility χ_m, and magnetic moments μ_{eff} values of square planar MPOCls have been investigated in the solid state over the range of 1.03–2.32 K Gauss and results are summarized in Table 1. The values reported in the table are the average of the three independent determinations. The experimental values reveals that CuPOCl and CoPOCl are paramagnetic and that of NiPOCl and ZnPOCl are diamagnetic. The observed magnetic moment values for CuPOCl and CoPOCI are higher than expected for $S=1/2$ spin state but less than their corresponding unsubstituted counterparts. Also, the μ_{eff} values of the complexes are found to vary with the strength of the applied magnetic field and this is due to the intermolecular cooperative effect [18].

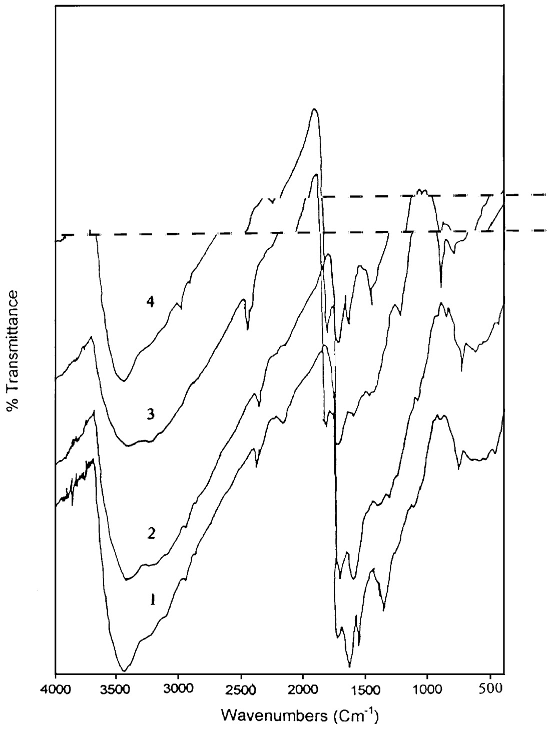


Fig. 3. IR absorption spectra of **1**. CoPOCl, **2**. ZnPOCl, **3**. CuPOCl and **4**. NiPOCl.

The observed higher values of magnetic moment at lower magnetic field strength may be due to the intermolecular magnetic interaction coupled with strong π-electron current of phthalocyanine molecule. Crystallographic studies [18] on phthalocyanines revealed that, during the process of stacking, each phthalocyanine molecule is stacked to the neighbouring molecule along the *b*-axis in such a way that each molecule is contributing either a nitrogen atom at a interplanar distance of 3.38Å above or below the central metal atom as shown in Fig. 2(a). Alternatively, it can also be placed one over the other with the separation of two molecules by a distance of 3.38Å above and below about the central metal atom [Fig. 2(b)]. This minimum interplanar distance seems to provide a suitable pathway for spin–spin coupling interaction between adjacent metal atoms either directly or super exchange through the N atoms of the molecule. The extent of super exchange interaction between the molecules depends primarily on the angle of inclination of the plane of the molecules, the type of metal atom, the nature of the substitutent and metal–metal distance. It seems the exchange interaction coupled with orbital contribution is the cause for the observed higher magnetic moments for CuPOC1 and CoPOCl at the lower magnetic field strength. But at higher magnetic fields, it seems molecules suffer tumbling, resulting in a decrease in intermolecular distance which in turn favours an effective intermolecular interaction. The hindered stacking in the above complexes is caused by the presence Cl substituted at the periphery of the molecule over the expected degree of Hall mobility.

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

Complex (yield) colour	Empirical 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 (Calc)
CuPcOCl	$C_{32}H_8N_8C1_8Cu$	1.03	+2263.0	2.35	C, 45.13, (45.09)
(90%)	(851.55)	1.30	+2074.0	2.25	H, 1.01, (0.94)
Dark green		1.51	+1610.0	1.98	N, 13.43, (l3.16)
		1.83	+1594.9	1.97	Cl, 33.46, (33.35)
		2.09	+1351.7	1.82	Cu, 7.46, (7.41)
		2.32	+1281.6	1.77	
CoPcOCl	$C_{14}HRN_8CI_8C0$	1.03	+2657.0	2.69	C, 45.72, (45.34)
(90%)	(846.93)	1.30	+2498.5	2.59	H, 1.08, (0.94)
Dark green		1.51	+2078.7	2.47	N, 13.43, (13.22)
		1.83	+1980.5	2.20	Cl, 33.69, (33.53)
		2.09	+1800.2	2.10	Co, 7.01, (6.96)
		2.32	+1690.1	2.09	
ZnPcOCl	$C_{32}H_8N_8CI_8Zn$	1.51	−1022.0	–	C, 45.58, (45.73)
(80%)	(853.38)				H, 1.07, (1.23)
Green with					N, 13.42, (13.38)
red tinge					Cl, 33.72, (33.13)
					Zn, 6.68, (6.53)
NiPcOCI	$C_{32}H_8N_5C_{15}Ni$	1.51	−660.5		C, 45.69, (45.35)
(90%)	(848.93)				H, 1.02, (0.94)
Dark green					N, 13.49, (13.23)
					Cl, 33.72, (33.54)
					Ni, 7.02, (6.93)

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

Complex	UV-visible Wavelength λ nm (log ε)	IR spectral data (cm^4)	Powder XRD data 2θ angle (d A)
CuPcOC1	241 (3.17)	757, 881, 1085, 1300, 1357, 1616, 2366, 3410.	26.88 (3.31)
	483 (1.67)		23.45 (3.79)
	642 (1.81)		25.48 (3.49)
	740 (1.44)		29.35 (3.04)
CoPcOCl	265 (3.22)	752, 886, 1088, 1316, 1388, 1610, 1706, 2929, 3400.	26.48 (3.36)
	479 (1.74)		23.92 (3.72)
	649 (1.34)		25.38 (3.51)
	733 (1.17)		20.35 (4.36)
ZnPcOCl	250 (3.14)	749, 880, 1082, 1342, 1610, 1726, 2356, 3408.	25.98 (3.43)
	525 (1.72)		24.48 (3.63)
	650 (1.79)		29.38 (3.04)
	750 (1.55)		20.43 (4.34)
NiPcOCl	232 (3.06)	772, 1072, 1345, 1539, 1616, 1714, 2852, 2924.	26.53 (3.36)
	470 (1.66)		23.37 (3.80)
	633 (1.70)		29.10 (3.06)
	725 (1.65)		22.81 (3.89)

6. Electronic spectra

The electronic spectra of octachloro substituted metal phthalocyanines are recorded in 18 M sulfuric acid and the results are tabulated in Table 1. For all the complexes, a peak in the range of 625–649 nm was observed and assigned to Q-band, attributed to $a_{1u} \rightarrow e_g$ transition. Peaks appears in the range 232–265 nm are attributed to C-band. The MPOCls that showed a peak in the range of 470–483 nm are assigned to B-band and are attributed to $a_{2u} \rightarrow e_g$. The peaks in the longer wavelength region 725–750 nm were observed for all the complexes′ bathochromic shift with respect to the corresponding parent phthalocyanines [19]. This is due to the presence of auxochrome Cl groups on the periphery of benzene portion of the complex.

7. Powder XRD

Powder XRD patterns of all MPOCls are taken in the range of 2θ, angle 5–60 (Table 2) showed identical features with very poor crystallinity. The patterns are qualitative and are similar to that of unsubstituted parent phthalocyanines. However the patterns are more dispersive in intensity for all the complexes than the corresponding metal phthalocyanines. The XRD patterns are used to explain qualitatively the degree of crystallinity.

8. Thermogravimatric analysis

All MPOCls have been studied thermogravimetrically in the atmosphere of nitrogen up to 850 °C. The data revealed that all complexes are stable up to 450 °C and show weight loss in the temperature range of 450–850 °C and the char yields are found to vary depending on MPOCl.

The Hall mobility due to interaction between the metal orbital and π-orbital of the neighboring phthalocyanine rings in their stacking demands relatively higher values of μ_{eff} for CuPOCI and CoPOCI over their unsubstituted counterparts. However, the experimental values of μ_{eff} for both complexes are found to be smaller than the corresponding unsubstituted metal phthalocyanines as observed in the literature [8]. This may be attributed to the influence of the final residue left over was found to agree well with the metal content. The observed stability in the nitrogen atmosphere is found to be ZnPOCl > NiPOCl > CoPOCl > CuPOCl.

9. Conclusions

A simple and convenient method has been optimized the synthesis of pigments 1,3,8,10,15, 17,22,24-octachloro phthaiocyanines of Cu (II), Co (II), Ni (II) and Zn (II). Magnetic susceptibility studies revealed the paramagnetic behavior of Cu (II) and Co (II) octachioro phthaiocyanine derivatives and the variation of magnetic moments with magnetic field indicated-the presence of intermolecular co-operative effect. Thermogravimetric analysis of the complexes in an inert atmosphere revealed the stability in the order ZnPcOCl > NiPcOCl > CoPcOCl > CuPcOCl.

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References

[1] Gregory P. Industrial applications of phthalocyanines. J Porphyrins and Phthalocyanines 2000;4:434.

[2] Venkataraman K. The chemistry of synthetic dyes. New York: Academic Press; 1952.

[3] Leznoff CC, Lever ABP. Phthalocyanines properties and applications, vol. 1. New York: VCH Publishers; 1989.

[4] Vartanyarn A.T.Zh. Fig Khim, 1948;22:769; Eley Nature (London)1948;162:819.

[5] Achar BN, Keshavayya J, Bhavanishankaragowda PS, Shankar Bhat S, Gopalamarthe K, Cletus JMD'souza. Biological Activity and staining property of metal phthalocyanine derivatives. Proc Indian, Natn Sci, Acad, Part B 1992;58(2-3):141–6.

[6] Achar BN, Bhandari JM, Urus HGVG. Histichemistry. A rapid saframin-metal phthalocyanine double staining technique for plants Biotechnic 1993;68(3):127–30.

[7] Somashekarappa MP. Studies on phtbalocyanine complexes. Doctoral thesis, Kuvempu University, Shankaraghatta, India, 2000.

[8] Keshavayya J, Studies on metal phthalocyanine complexes. Doctoral thesis, Mysore University, Mysore, India, 1988.

[9] Venugopala Reddy KR, Keshavayya J. Synthesis and magnetic, spectral and thermal studies on 1,3,8,10,15,17, 22,24-octanitrophthalocyanines. Turk J Chem 2002;26(4):573–80.

[10] Venugopala Reddy KR, Keshavayya J. Synthesis, Magnetic, spectral and thermal studies on metal(II)-1,3,8,10,15,17,22,24-octaaminophthalocyanines. Synth React Inorg Metal-Org Chem 2002;32(7):1235–44.

[11] Venugopala Reddy KR, Keshavayya J. Synthesis of symmetrically substituted octabromophthalocyanine pigments and their characterization. Dyes and Pigments 2002;53: 187–94.

[12] Klyner VN, Shiyaera LSIzv, Vyssh-Ucheb Zaved. Direct synthesis of chloroderivatives of metal phthalocyanines. Khim Khim Tekhnol 1969;12(6):774–5.

[13] Vogel's textbook of practical organic chemistry, Vth ed. Longman Group UK; 1989.

[14] Selwood P. Magnatochemistry. 2nd ed. New York: Interscience; 1952.

[15] Somashekarappa MP, Keshavayya J. Synthesis, Magnetic, spectral and thermal studies on metal (II) l,8,15,22-tetranitrophthalocyanines. Synth React Inorg Metal-Org Chem 1999;29(5):767–83.

[16] Silverstein, Bassler and Morrill. Spectroscopic identification of organic compounds. Vth ed. John Wiley Publications; 1991.

[17] Somashekarappa MP, Keshavayya J. Synthesis and structural studies of metal (II) 1,8,15,22-phthalocyaninetetraamine. J Saudi Chem Soc 1999;3(2):113–9.

[18] Achar BN, Bhandari JM. Magnetic properties and ESR studies on copper phthalocyanine. Synth React Inorg Metal-Org Chem 1993;23(1):133–48.

[19] Achar BN, Fohien GM, Parker JA, Keshavayya J. Synthesis and structural studies of metal (II)-4,9,16,23 phthalocyanine tetraamines. Polyhedron 1987;6(6):1463–7.