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RESEARCH LETTER

One pot and solvent-free synthesis of 2,9,16,23-tetrachlorometal(II) phthalocyanines

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A novel one pot and solvent-free synthesis of 2,9,16,23-tetrachloro metal(II)phthalocyanines in microwave using monosodium salt of 4-chlorophthalate as starting material is described. This method in comparison to conventional route offers high yields (75–92%), eliminates the use of toxic organic solvents, reduces multistep synthesis to one-step, reaction temperature from 190 to 120°C, and reaction time from 5–6 hours to 5 minutes.

Keywords: one pot; solvent-free; microwave; tetrachlorometal(II) phthalocyanines

Introduction

Metallophthalocyanines are extremely versatile materials with numerous fascinating properties (1). Phthalocyanines were one of the first man-made macrocycles that were synthesized and used as model compounds to mimic the biologically important porphyrins (2). Recently, there has been a renewed interest in phthalocyanine chemistry, as phthalocyanines and their derivatives find commercial applications as dyes and printing inks (3), toners in color photocopiers and laser printers (4), optical data storage systems (5), photovoltaic materials in solar cells (6), materials for fabrication of light emitting diodes (LED) (7, 8), nonlinear optical materials (9–12), photoconductors in xerography (13), differential staining agents (14), gas diffusion electrodes (15), liquid crystals (16–18), photosensitizers in treatment of cancer (19–22), active compounds in gas sensing systems (23, 24), electrochromic substances (25), and in diverse catalytic systems (26–28). These versatile features have stimulated efforts for the synthesis of new phthalocyanine derivatives with the purpose of developing new materials comprising improved functional characteristics.

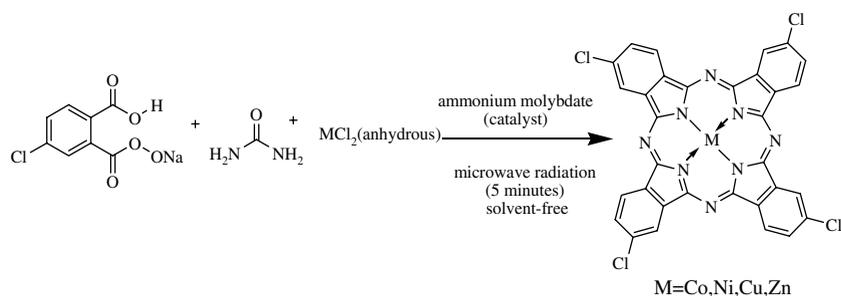
Conventional synthesis of tetrachlorometal(II) phthalocyanines involves multistep route in which firstly tetranitrometal(II)phthalocyanines are prepared by heating a mixture of 4-nitrophthalic acid, ammonium chloride, ammonium molybdate, and excess urea in nitrobenzene, which are then converted to tetraaminometal(II) phthalocyanines followed by modified Sandmeyer's reaction to form corresponding

tetrachlorometal(II) phthalocyanines (29, 30). These reported methods of preparation are associated with several limitations such as low yield, use of toxic and high boiling solvent (nitrobenzene), stringent reaction conditions, and long reaction time of 5–6 hours. The present work describes one pot and solvent-free synthesis of high purity 2,9,16,23-tetrachlorometal(II) phthalocyanines (MPcCl) from monosodium salt of 4-chlorophthalate which is an economical phthalocyanine precursor. The products can be recrystallized by using conc. H₂SO₄ but due to its hazardous nature its use was circumvented, and we obtained the highly pure products (as depicted in elemental analysis) by just washing. Short reaction time, high yield, solvent-free synthesis, high atom economy, mild reaction conditions, and use of microwave technology as a non-polluting mode of activation are the advantages of present protocol which leads to the development of clean and environmentally benign procedure.

Results and discussion

The solvent-free method adopted for the direct synthesis of 2,9,16,23-tetrachlorometal (II) phthalocyanines in one pot using microwave involves cyclotetramerization of 4-chlorophthalate in presence of urea as the source of nitrogen, in which template effect is afforded by a suitable metal cation (Scheme 1). The use of ammonium molybdate [Mo₇O₂₄(NH₄)₆·4H₂O] as a catalyst results in maximum utilization of starting materials, and the amount of energy used is also minimized (31). The excess of 4-chlorophthalate and metal-free phthalocyanine formed are easily

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Scheme 1. One pot and solvent-free synthesis of 2,9,16,23-tetrachlorophthalocyanato metal(II).

removed by washing the product. The complexes synthesized have metallic luster and are deep bluish-green except 2,9,16,23-tetrachlorozinc(II)phthalocyanine which has a greenish-brown tinge. All these complexes are insoluble in water and organic solvents, such as ethanol, carbon tetrachloride, benzene, diethyl ether, chloroform but highly soluble in *N*-methyl-2-pyrrolidinone and concentrated sulphuric acid and partially soluble in DMF, DMSO, and pyridine. The one pot synthesis method offers the advantages of higher yields, short reaction times, easy workup, and also there is no wastage on account of the ligand synthesis. The microwave irradiation accelerates the cyclotetramerization process and reduces the reaction time and energy input compared to conventional heating method. On the other hand, the use of solvent-free system in which microwaves interact directly with the reagents can more efficiently drive the chemical reaction toward completion. These advanced reaction conditions reduce the cost of production of commercially important phthalocyanine complexes.

The elemental analyses of C, H, and N for all the complexes agreed fairly well with the calculated values. The metal content incorporated in the phthalocyanine complex was determined using atomic absorption spectrometer. Since these complexes were not soluble in water, demetallation was done first by digestion of 5.0 mg of complex in 10 mL of nitric acid in a microwave digester system for 10 minutes and then diluted sufficiently by double-distilled water. Analytical results of the metal content agreed well with the calculated values.

The electronic spectra of the complexes were recorded in the concentration range of 1×10^{-4} M in *N*-methyl-2-pyrrolidinone as the solvent (Figure 1). For all these complexes the absorption bands observed at 675–680 and 608–620 nm are attributed to characteristic Q-bands of phthalocyanine ring arising because of $a_{1u} \rightarrow e_g$ transitions. Unlike parent phthalocyanines these complexes exhibited split bands rather than a single band, which are in accordance with the literature (32). A sharp intense

B-band is observed for all the complexes in the range of 440–445 nm which is assigned to $a_{2u} \rightarrow e_g$ transitions of the phthalocyanine molecule. These two bands, B and Q, are, respectively, characteristic of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in phthalocyanines (33). Comparing the width of the Q-bands, a charge transfer transition is suspected in CuPcCl, CoPcCl, and NiPcCl. The observed wider Q-band peaks for these complexes over those of ZnPcCl noticeably reflects the overlapping between $\Pi \rightarrow \Pi^*$ and charge transfer transitions (34).

Infrared (IR) spectra of all the complexes were recorded in KBr pellets and the plots are given in Figure 2. A broad absorption band was observed for all these complexes in the range of 3317–3448 cm^{-1} and may be attributed to the presence of hydrogen bonding formed between the H-atom of moisture

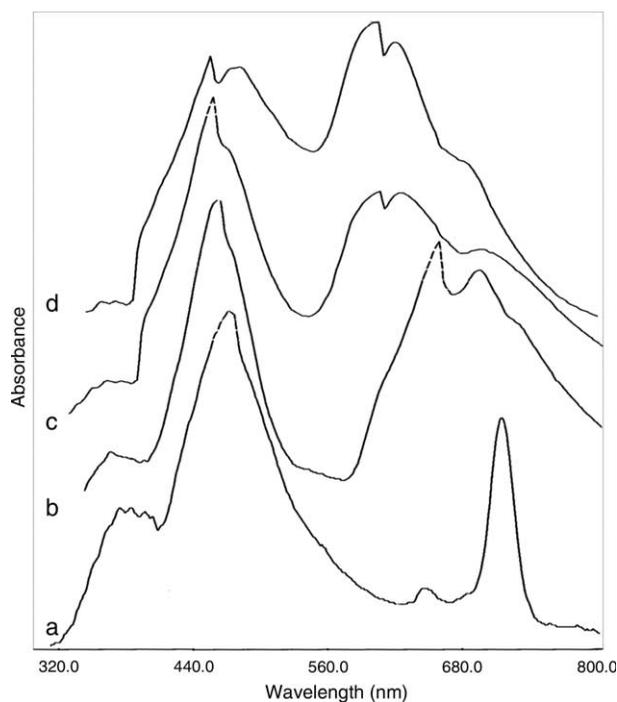


Figure 1. UV-visible absorption spectra of (a) ZnPcCl, (b) CoPcCl, (c) CuPcCl, and (d) NiPcCl.

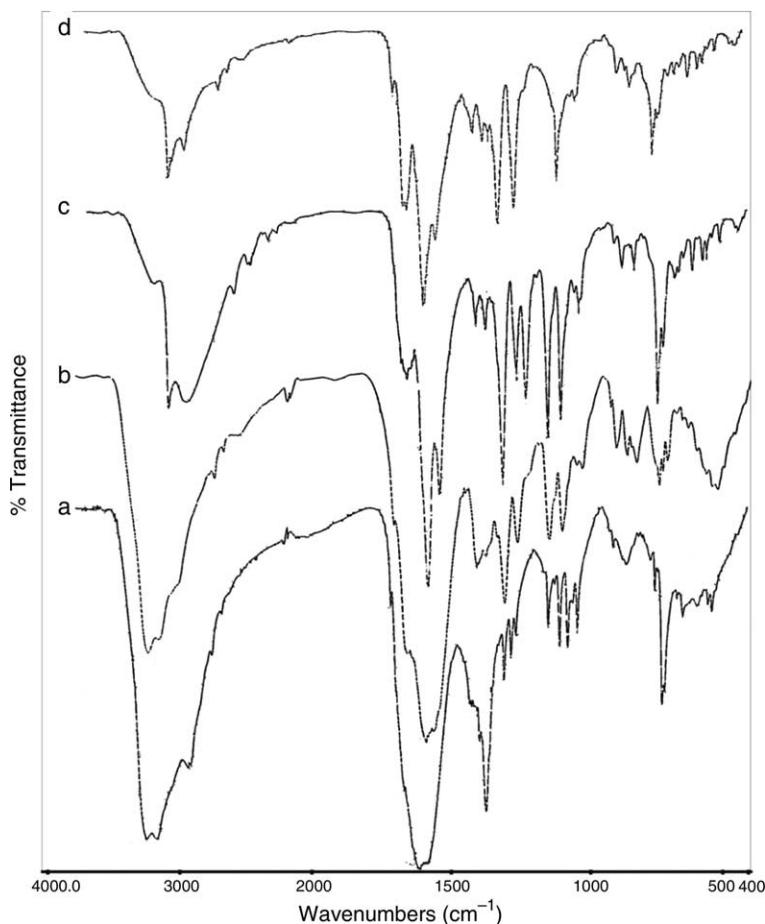


Figure 2. IR absorption spectra of (a) CuPcCl, (b) ZnPcCl, (c) CoPcCl, and (d) NiPcCl.

observed on the KBr pellets and the N-atom of the phthalocyanine molecule during pelletization (35). The sharp peaks at $1648\text{--}1655\text{ cm}^{-1}$ are assigned to C=C and ring (skeletal band) stretching. The peaks at $1333\text{--}1360\text{ cm}^{-1}$ are due to C–N aromatic stretching vibrations. The absorption bands that appeared around $751\text{--}758\text{ cm}^{-1}$ are assigned to C–Cl stretching frequency of the peripheral substitution on the ring. All other remaining peaks that appeared around $840\text{--}866$ and $1127\text{--}1166\text{ cm}^{-1}$ are attributed to the various skeletal vibrations of phthalocyanine ring (36).

All these complexes have been studied thermogravimetrically in the atmosphere of nitrogen up to 600°C . Thermograms (Figure 3) of all the complexes revealed that weight loss in the range of $50\text{--}140^\circ\text{C}$ may be attributed to the loss of moisture present in them. The second weight loss of about 20% after 200°C corresponds to the loss of chloro functional groups present in the periphery of the molecule. The major weight loss was observed in the temperature range of $400\text{--}600^\circ\text{C}$ corresponding to the degradation of phthalocyanine moiety. The observed thermal

stability of the complexes is in the order $\text{CuPcCl} > \text{CoPcCl} > \text{NiPcCl} > \text{ZnPcCl}$.

Experimental section

One pot and solvent-free synthesis of 2,9,16,23-tetrachlorometal(II) phthalocyanines under microwave radiations

The mixture of urea (15 mmol), monosodium 4-chlorophthalate (4 mmol), anhydrous metal chloride (1 mmol) and ammonium molybdate (0.05 mmol) were ground together in agate mortar and pestle and then placed in a microwave pressure vessel and irradiated in the microwave reactor at power of 400W for 5 minutes at 120°C . After completion of reaction, the green colored solid obtained was ground and washed with acetonitrile, sodium hydroxide (1.0 M), distilled water, hydrochloric acid (1.0 M), and then again with distilled water until the pH of the filtrate became neutral. After drying under reduced pressure, the pure product was analyzed. The complexes were characterized by elemental analysis, IR, thermogravimetric analysis (TGA), and UV/Vis techniques.

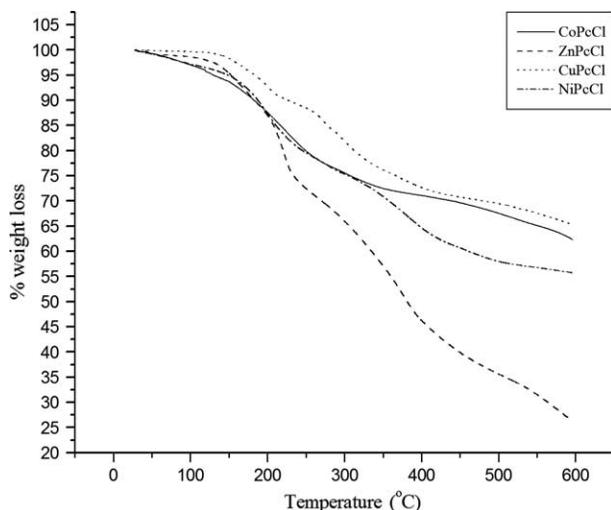


Figure 3. TGA curves of tetrachlorometal(II) phthalocyanines.

Cobalt (II) tetrachlorophthalocyanine, CoPcCl

Anal. Calc. for $C_{32}H_{12}N_8Cl_4Co$ (formula weight = 709.24): C 54.1, H 1.6, N 15.8, Co 8.3. Found C 54.2, H 1.8, N 15.7, Co 8.2, Yield: 88%, mpt. $>300^\circ C$, λ_{max} (*N*-methyl-2-pyrrolidinone)/nm: 346, 445, 640, 680, ν_{max}/cm^{-1} : 3323, 1648, 1356, 1130, 840, 751.

Nickel (II) tetrachlorophthalocyanine, NiPcCl

Anal. Calc. for $C_{32}H_{12}N_8Cl_4Ni$ (formula weight = 709.00): C 54.2, H 1.7, N 15.9, Ni 8.2. Found C 54.2, H 1.8, N 15.7, Ni 8.1, Yield: 90%, mpt. $>300^\circ C$, λ_{max} (*N*-methyl-2-pyrrolidinone)/nm: 348, 445, 597, 611, ν_{max}/cm^{-1} : 3317, 1651, 1359, 1127, 840, 750.

Copper (II) tetrachlorophthalocyanine, CuPcCl

Anal. Calc. for $C_{32}H_{12}N_8Cl_4Cu$ (formula weight = 713.85): C 54.1, H 1.5, N 15.6, Cu 8.3; Found C 54.0, H 1.6, N 15.7, Cu 8.1, Yield: 92%, mpt. $>300^\circ C$, λ_{max} (*N*-methyl-2-pyrrolidinone)/nm: 350, 445, 596, 617, 690, ν_{max}/cm^{-1} : 3429, 1654, 1333, 1165, 865, 755.

Zinc (II) tetrachlorophthalocyanine, ZnPcCl

Anal. Calc. for $C_{32}H_{12}N_8Cl_4Zn$ (formula weight = 715.69): C 53.9, H 1.6, N 15.6, Zn 5.41, Found C 54.2, H 1.8, N 15.7, Zn 5.38, Yield: 75%, mpt. $>300^\circ C$, λ_{max} (*N*-methyl-2-pyrrolidinone)/nm: 355, 440, 608, 675, ν_{max}/cm^{-1} : 3447, 1654, 1352, 1131, 843, 757.

Measurements

SL-159 ELICO spectrophotometer, with matched 1 cm silica cells from Elico Ltd, India, was used to

obtain the electronic spectra in the region 200–900 nm in *N*-methyl-2-pyrrolidinone as a solvent. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer spectrometer at room temperature using KBr pellet technique. The pellet was used to record the IR spectrum in the range of 4000–400 cm^{-1} under the atmospheric conditions with a resolution of 1 cm^{-1} . Carbon, hydrogen, and nitrogen analyses were performed at elemental Analysensysteme GmbH VarioEL V3.00. Anton Paar multiwave 3000 microwave reaction system has been used for activating the reaction as well as for sample preparation (digesting a known amount of complex) for metal analysis. The amount of metal incorporated into phthalocyanine complex was detected successfully by using Labindia atomic absorption spectrometer.

Conclusions

We have developed an efficient, economical, rapid and green protocol for the direct synthesis of 2,9,16,23-tetrachlorometal(II) phthalocyanines using microwave under solvent-free conditions. The wastage on account of the ligand synthesis is minimized since the process was carried out in one pot i.e. there is an in-situ generation of the ligand from the starting materials followed by the insertion of metal to form a complex. Thus, this method in comparison to conventional route offers high yields, milder reaction conditions, shorter reaction time, eliminates the use of toxic organic solvents, and reduces multistep synthesis to one step only.

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