Indian Journal of Chemistry
Vol. 32A, December 1993, pp. 1029-1033

Synthesis of soluble phthalocyanines and study of their aggregation behaviour in solution

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Received 9 March 1993; revised and accepted 6 July 1993

Aryloxy substituted soluble phthalocyanine (Pc) and its metal complexes ($MPcX_4$, X = 4-ethylphenoxy, M = 2H, Cu, Ni, Zn, Fe, Co) have been synthesized and characterized by elemental analysis, ^1H NMR, UV—visible and IR spectroscopy. Degree of association in toluene solution has been measured by molecular weight determination using vapour pressure osmometry. Association and its relative order have also been established in these complexes by UV-visible spectral studies.

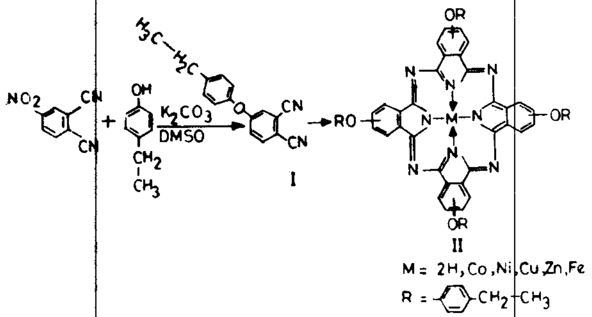
Phthalocyanine (Pc) compounds have been widely studied for over 50 years[1] due to their varied applications. There has been much excitement recently concerning the use of phthalocyanines in a host of new applications such as electrocatalysts for four-electron reduction of oxygen to water[2], chemical sensors[3], photo-sensitive materials for photodynamic therapy[4], in discotic mesophase formation[5], in addition to their intrinsic uses as dyes, pigments and in photocopying devices. The exceptionally high thermal and chemical stability of the phthalocyanine core gives rise to a vesatile chemical system. The synthesis of a variety of peripherally tetra- and octa- or higher order of four-substituted phthalocyanines, both metallo and non-metallo, have been reported[1,6]. Insolubility in most common organic solvents is a characteristic property of peripherally unsubstituted phthalocyanine and its numerous metal complexes; therefore, the main aim of these substitutions has been to enhance phthalocyanine's very limited solubility, which facilitates its purification and spectroscopic characterization. The discovery of soluble phthalocyanines should lead to significant advances in areas like biological modelling and homogeneous catalysis. The prospect of obtaining highly ordered thin films of phthalocyanine using Langmuir-Blodgett technique from organic solvent-soluble phthalocyanines[3,7a,8] for the development of phthalocyanine-based gas sensor and electronic devices, and its superiority over the other techniques like vacuum sublimation, spraying of a fine suspension, dispersion in a polymeric binder and mechanical rubbing, which are applied in the case of insoluble phthalocyanines, has further generated interest in the synthesis of soluble phthalocyanines.

In the present work we report the synthesis and characterization of a soluble phthalocyanine compound with tetra-aryloxy substitution and its complexes with some transition metal ions. Most of the reports available in literature are on the synthesis of alkoxy substituted soluble phthalocyanines. Reports on aryloxy substituted phthalocyanines are scanty and most of these are patented. Phenoxy substituted phthalocyanines are known[9], but of these only cumyl phenoxy phthalocyanines[7] have been reported. In an endeavour to extend the range of available soluble substituted phthalocynines, we have chosen a small substitutent, viz., ethyl, instead of cumyl.

The approach based on synthesis of phthalocyanine compounds (metal-free and metal-containing) with aryloxy group as substituent at the periphery appears to be promising because it has been established that the bulky substituents[10] as well as substituents attached to the periphery by flexible oxygen bridge, increase solubility of phthalocyanine derivatives. The greater solubility will facilitate purification and spectral study as well as determination of molecular association in solution by spectroscopy and vapour pressure osmometry (VPO) measurements. Also, the aromatic substitutent attached through oxygen as the bridging atom, which is known to permit electron delocalization, will increase the number of conjugated electrons and can enhance electrical conductivity as well as electrocatalytic activity[2].

Materials and Methods

All the reagents and solvents used were reagent grade commercial samples. These were used without further purification unless otherwise noted. 4-Nitrophthalonitrile was prepared by the method reported by Leznoff *et al.*[11] 4-(4-Ethylphenoxy)phthalonitrile(I) was prepared by the base catalysed nucleophilic aromatic nitro displacement[9,12] of 4-nitrophthalonitrile with 4-ethylphenol. The tetrakis (4-ethylphenoxy)phthalocyanine compounds ($MPcX_4$) were synthesized according to the Scheme 1. H_2PcX_4 was synthesized by reacting(I) with stoichiometric quantity of hydroquinone as a uniphase fused melt in a sealed tube following a method reported by Snow and Jarvis[7a] for metal-free phthalocyanine, whereas the metal complexes were synthesized by a modification of the method followed by Snow and Jarvis[7a]. $MPcX_4$ (M = Co, Ni, Cu, Zn, Fe) were synthesized by reacting(I) with respective metal powder in the presence of catalytic amount of ammonium molybdate in a sealed tube. All the prepared phthalocyanines were purified by column chromatography and by Soxhlet extraction. Molecular association of the $MPcX_4$ compounds in toluene solution was measured by classical molecular weight determination using vapour pressure osmometry. The UV-visible spectra were recorded in dry toluene solution in the concentration range 5×10^{-4} *M* to 4×10^{-5} *M*.



Scheme 1

Synthesis of 4-(4-*ethylphenoxy*) *phthalonitrile* (*I*)

In a 250 ml R.B. flask, 4-nitrophthalonitrile (6.92 g, 40 mmol), 4-ethylphenol (4.88 g, 40 mmol) and anhydrous potassium carbonate (8.28 g, 60 mmol) were stirred at room temperature (25°C) under nitrogen atmosphere in 60 ml of dry DMSO for 36 hr. Potassium carbonate was added in five portions at 1 hr intervals. The reaction was worked up by filtering the undissolved potassium carbonate and adding the filtrate to 200 ml cold water with stirring. The crude product was extracted using 200 ml dichloromethane in three lots. The dichloromethane solution was then washed with 100ml 5% Na_2CO_3 solution (to remove unreacted phenol) followed by distilled water. After drying the dichloromethane solution over Na_2SO_4, the solvent was evaporated whereby the nitrile was obtained as a viscous oil. Stirring the oil with hexane for 2 hr and leaving it in a freezer overnight resulted in the formation of white crystals (6.75g, 68% yield), m.p. 66°C, IR(KBr): ν(CN) 2246cm^{-1}. ^{1}H NMR ($CDCl_3$): δ1.35-1.20 ppm (t,3H,CH_3), δ 2.81-2.58 ppm (q,2H,CH_2), δ7.76-6.94 ppm (m,7H,arom). Anal.: Found: C,77.53; H,4.78; N, 11.24. Calc. for $C_{16}H_{12}N_2O$: C, 77.42; H, 4.85; N, 11.29%.

Synthesis of phthalocyanines

H_2PcX_4 was prepared by mixing 1.49 g (6 mmol) of (I) and 0.16 g (1.50 mmol) of hydroquinone in a tube. The mixture was fused by gentle heating, cooled, and the tube was sealed *in vacuo*. The entire tube was then heated at 175°C with stirring for 14 hr. The metal complexes $MPcX_4$ were prepared by reacting (I) with the respective metal powders in 1:2 molar ratio in the presence of catalytic amount of ammonium molybdate in a sealed tube at 220-250°C for 12 to 40hr (exact reaction times and reaction temperatures are given in Table 1). In all the cases the crude product was purified by column chromatography on neutral alumina using THF as eluent. The eluted solution was concentrated and reprecipitated in methanol by drop-wise addition and stirring. The precipitate was filtered and was further purified by extracting with methanol using a Soxhlet extractor to remove unreacted phthalonitrile (I).

Results and Discussion

For the synthesis of substituted phthalocyanines one starts with the substituted dicyano derivatives; in the present case, this derivative was 4-(4-ethylphenoxy)phthalonitrile (I). This new hitherto unreported derivative was obtained in 68% yield by anhydrous potassium carbonate catalysed nitro displacement[9,11-14] and the product was characterized by elemental analysis, ^{1}H NMR and IR spectroscopy. While the H_2PcX_4 was prepared by a reported method using hydroquinone as catalyst, for the synthesis of metal phthalocyanines we modified the method, reported by Snow and Jarvis[7a]. The modification simply involved incorporation of catalytic amount of ammonium molybdate, but this facilitated the occurrence of reactions under milder conditions at lower temperatures and in lesser

Table 1—Spectroscopic and analytical data for phthalocyanines with reaction time and temperature

Pc/Mpc	Anal. Found (calc.) %			Reaction Time/Temp.	UV/Vis. $\lambda_{max(nm)}$	IR (cm^{-1})	$^1H_{NMR}$ ($CDCl_3$) δ in ppm	Yield (%)
	C	H	N	hr °C				
H_2PcX_4	75.85 (77.25)	4.79 (5.06)	10.80 (11.26)	14/175	285,339, 604,636, 664,699	743s,764m, 823m,936m, 1034s,1089m, 1170m,1230s, 1475m,1506s, 1616m,2859w, 2931w,2965m, 3293m.	-5.83 (br, $-$NH,2H) 1.45-1.32 (t,CH_3,12H) 2.98-2.67 (q,CH_2,8H) 7.95-7.08(m,arom28H)	45
$CuPcX_4$	71.48 (72.75) 5.89	4.19 (4.57) (6.01)	9.97 (10.60) Cu	12/220	283,345, 610,679	702s,747s, 825m,844m, 956m,1039w, 1068m,1099m, 1118w,1164m, 1237s,1474m, 1509s,1606s, 2886w,2934w, 2974w,3049w.	1.32-1.12 (t, $-CH_3$, 12H) 2.77-2.50 (q, $-CH_2$,8H) 7.65-7.04 (m,arom, 28H)	73
$ZnPcX_4$	71.89 (72.62) 6.02	4.38 (4.57) (6.17)	9.81 (10.51) Zn	36/240	290,351, 612,679	751s,777m, 828m,960w, 1039m,1052m, 1098m,1119m, 1175m,1235s, 1416m,1475s, 1505s,1602s, 2930w,2968m, 3032w,3061w		48
$FePcX_4$	72.41 (73.28) 4.88	4.38 (4.61) (5.32)	10.14 (10.68) Fe	40/250	347,605, 637,666	701s,749s, 830m,951w, 1038m,1062m, 1098m,1062m, 1167m,1234s, 1411m,1475s, 1509s,1606s, 2930w,2968m, 3029w.		15
$CoPcX_4$	72.39 (73.07) 5.33	4.09 (4.60) (5.60)	9.84 (10.65) Co	14/230	283,334, 602,670	754s,827s, 962m,1034m, 1072m,1104m, 1119w,1166m, 1235s,1409m, 1475s,1509m, 1609s,2930w, 2967m,3033w.		41
$NiPcX_4$	72.71 (73.08) 5.24	4.09 (4.60) (5.58)	9.29 (10.65) Ni	40/250	291,331, 606,669	754s,780s, 827m,961w, 1038m,1099m, 1122m,1176m, 1232s,1420s, 1474s,1505s, 1601s,2930w, 2970m,3032w.		35

reaction time (Table 1). In the present case, generally, higher yields of metal phthalocyanines were obtained; in one case, namely, $CuPcX_4$ the yield was 73%. All the phthalocyanines, metal-free and metal-containing, are soluble in benzene, toluene, dichloromethane, chloroform, THF, dioxane, etc. Elemental analyses are consistent with the assigned formulations except in the case of iron complex where the percentage of iron found was slightly low. Spectroscopic data (^1H NMR, IR and electronic) are also consistent with the assigned structure (II). The IR spectrum of H_2PcX_4 exhibited N-H absorption at 3293 cm^{-1}, characteristic of N-H stretching of metal-free phthalocyanines[15] which disappeared on the formation of its metallated derivatives. The C-O-C ether linkage was also evident in all the compounds (1230-1237 cm^{-1}). IR spectra of the phthalocyanines are indicative of their purity as shown by the absence of the carbonyl and nitrile absorptions which usually arise due to unreacted nitrile or byproducts.

The ^1H NMR spectrum of H_2PcX_4 exhibited a broad absorption for the internal NH protons at -5.83 ppm when the spectrum was run at high concentration. The value is comparable in general to those obtained for phenoxy, cumylphenoxy and other tetra-substituted phthalocyanines[7a,9,12b,14]. The absorption changed from -5.83 to -5.19 ppm on dilution; such an observation indicates that at higher concentration aggreagated phthalocyanine species exist[14a,16] and this reinforces the ring current of the monomer, and shifts the cavity proton resonance to high upfield value[17,18] which on dilution dissociate into monomers. This type of change in chemical shift has been also observed in the case of porphyrins[19].

The molecular weight measurements were carried out at one concentration (1×10^{-2} *M*) for each of the phthalocyanines and at different concentrations in the range 1×10^{-3} *M* to 2×10^{-2} *M* for three of the phthalocyanines $MPcX_4$ (M = 2H, Cu, Co). The number average degree of association (α) was calculated for each of the complexes at one concentration (10^{-2} *M*), the values obtained were 2.11, 3.31, 3.97, 1.82, 4.13, 2.21 for 2H, Cu, Ni, Zn, Fe and Co complexes, respectively. These values indicate that Ni and Fe complexes exist mainly as tetramers, Cu as trimer, and Co, Zn and the metal-free phthalocyanines as dimers under these conditions. It was also noted that change in concentration (2×10^{-2} *M* to 1×10^{-3} *M*) does not significantly change the value of α in the cases of Cu (α varies from 3.27 to 3.31), Co and the metal-free complexes (α varies from 1.82 to 2.21). The values of the degree of association observed for the 4-ethylphenoxy complexes are similar to those observed by Snow and Jarvis for the corresponding cumylphenoxy complexes[7a]. Such a similarity is unexpected in view of the report[21a] that the degree of association is affected by the bulkiness of peripheral substituent; however, there may be an optimum size upto which such an effect may be observed and beyond which the increase in size may not change the degree of association. To verify this studies ought to be done on other phenoxy substituted phthalaocyanines. It is interesting to note that change in the metal ion of the phthalocyanine complexes changes the degree of association in solution dramatically. For example Co, Ni, Cu complexes exist mainly as dimer, tetramer and trimer respectively. Thus, it is apparent that the nature of the metal ion affects the degree of association, but it is not clear in what way this effect arises. Snow and Jarvis[7a] have tried to explain the high value of nickel cumylphenoxy phthalocyanine on the basis of the d^8 configuration of Ni(II) but the variation due to other metal ions has not been commented upon. In our case we have found that the complex of iron(II), a d^6 ion, has the same value of $\alpha(\backsim 4)$ as the complex of nickel(II) which has d^8 configuration.

The electronic absorption spectra of all the complexes exhibit a strong and narrow absorption between 670 and 701 nm which is due to π-π^* transition and is commonly referred to as Q band. It is accompanied by a weaker satellite band which is 60 to 70 nm shorter in wavelength, and a second intense and broad π-π^* transition in the range 331-351 nm, called soret or B band. These bands are characteristic of monomeric phthalocyanines[20,21a]. As expected, the metal-free species H_2PcX_4 shows two closely spaced Q bands because of its lower (D_{2h}) symmetry[20]. Another broad and partially resolved π-π^* absorption band appears between the first strong π-π^* absorption and the satellite band. The presence of this broad band is indicative of molecular association in solution. This band is attributed to the associated phthalocyanine species[21] which arises due to exciton splitting of the excited state and, further, its intensity is related to the degree of association[21]. In the present case, intensity of this partially resolved band is higher for the Ni and Fe complexes as compared to that for Cu complex which in turn is higher than that for metal-free, Co and Zn complexes at the same concentration of the solution, indicating that the degree of association in solution decreases in the order Ni, Fe > Cu > 2H, Zn, Co complex. This order of degree of association is in agreement with the conclusion drawn from the molecular weight data discussed earlier.

UV-visible spectra for the phthalocyanines were also recorded at different concentrations. It was observed that although the spectral pattern remains the same, the intensity of band arising due to the associated species is high and the Q band is slightly broadened and also blue shifted in the case of the solutions of higher concentrations. These observations are indicative of increase in the degree of association of the phthalocyanines at higher concentrations as compared to that in dilute solution.

Acknowledgement

One of the authors (R.S.) is grateful to the UGC, New Delhi for financial assistance.

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