

Mild Synthesis of Metallophthalocyanines

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Abstract

Phthalocyanines have been synthesized via several procedures, although most methods utilize vigorous reaction conditions. A mild synthesis of metallophthalocyanines has been conducted from 1,2-dicyanobenzenes upon treatment with a metal salt and triethylamine in methanol at reflux (65 °C). This method has been used to prepare a wide assortment of metallophthalocyanines as well as several substituted copper-phthalocyanines.

Key words: complexes, copper, phthalocyanine, triethylamine

1-Introduction

Phthalocyanines are aromatic macrocyclic compounds that are extensively used as green and blue dyes.¹ These compounds and their derivatives have several important uses² such as in optical materials,³ organic semiconductors,⁴ applications in gas sensors⁵ and pH sensors,⁶ liquid-crystal displays,⁷ and more recently as catalysts in organic transformations.⁸ Traditionally, the synthetic routes to produce phthalocyanines have been via extremely rigorous reaction conditions. Many preparative methods according to literature include limitations such as extreme heating (up to 300°C) or utilizing strong bases.⁹ More recently, mild conditions have been recently reported from phthalimides or dicyanobenzenes, but only at temperatures as low as 100°C.^{2a,10} In this manuscript we report a new suitable method for transforming 1,2-dicyanobenzenes into phthalocyanines through the treatment of these 1,2-dicyanobenzenes with metal salts and triethyl amine under the mildest conditions reported thus far.

2-Results and Discussion

The preparation of copper phthalocyanine from 1,2-dicyanobenzene under various reaction conditions was initially investigated. (Results are summarized in Table 1). Beginning with copper(II) acetate, the equivalents of the triethylamine used in the reaction were varied at 65°C (entries 1-4), with the optimum result being 5.0 equivalents (39%, entry 1). The reaction yields were significantly lowered under elevated temperatures in either ethanol (78°C) or neat triethylamine (89°C), with yields of 21% and 0% respectfully (entries 5 and 6). Increasing reaction time from 24 to 48 hours with 5.0 equivalents of triethylamine at 65°C substantially increased the yield from 39% to 74% (entries 1 and 8). Further increasing reaction time to 72 hours, however, did not have a significant effect on the yield (entries 8-9). Interestingly, this reaction was successful at room temperature, but only after constant stirring for 8 weeks, with a yield of 42% (entry 7). This study was followed by evaluating the reaction under the established optimum conditions using various copper salts to observe how the counter anion affected the yield (entries 8 and 10-14). With its 74% yield, copper(II) acetate still proved to be the most effective salt (entry 8).

Other transition metal salts were also investigated, primarily the acetate varieties such as Mn(OAc)₂, Co(OAc)₂, and Zn(OAc)₂.

Here, various metal phthalocyanines were accessed quite easily utilizing this new synthetic method (entries 15-22).¹¹ Even a phthalocyanine of a main group metal could also be effectively synthesized, as magnesium phthalocyanine was produced in entry 23.

To increase the viability of this new method, substituted 1,2-dicyanobenzenes were utilized. These substituted 1,2-dicyanobenzenes were either purchased through chemical suppliers or synthesized by the procedure by Wohrle *et. al.*¹²

With the substituted 1,2-dicyanobenzenes in hand, the optimized reaction conditions were used to synthesize substituted copper phthalocyanines (Table 2). Each time the procedure was successful, furnishing the corresponding copper phthalocyanine. In every reaction, the yields were high with the exception of the reaction from 4-methyl-1,2-dicyanobenzene to yield compound **4**. A possibility for this lower yield could be due to the fact that these compounds had much lower solubilities in methanol than their counterparts in the table.

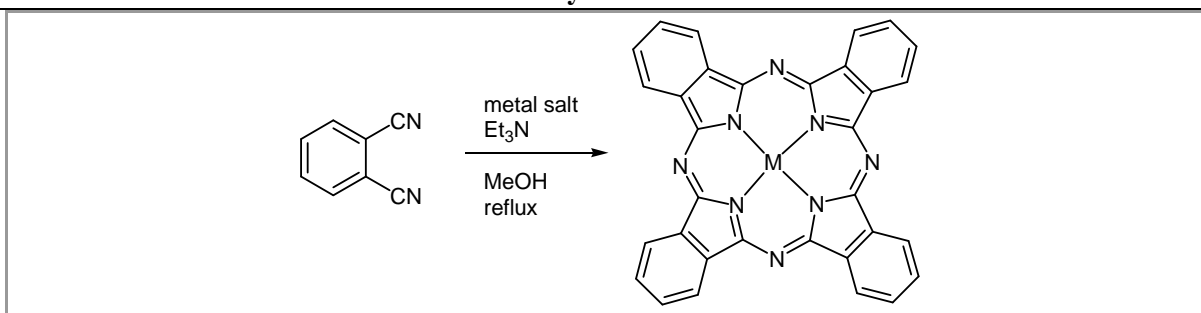
3-Conclusions

In conclusion, we have described a new method for the synthesis of metallophthalocyanines from 1,2-dicyanobenzenes using triethylamine and metal salts under the mildest conditions reported thus far. The advantages of utilizing this new method are the extremely low cost and mild reaction conditions. The simplicity of the reaction is an additional advantage, as several novice undergraduates were able to conduct and repeat the procedure. Current studies are employing this synthesis to cheaply and quickly yield metallophthalocyanines to be used as catalysts in cyclopropanation reactions from diazo compounds. We would also like to study this reaction to potentially produce similar complexes such as subphthalocyanines and superphthalocyanines.¹

4-Acknowledgments

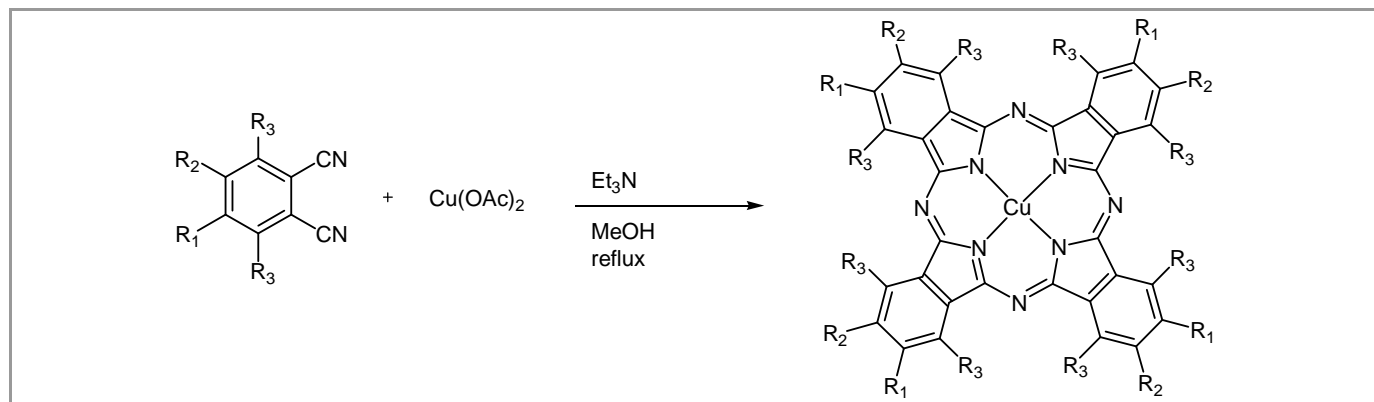
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Table 1 Synthesis of Metallophthalocyanines from 1, 2-Dicyanobenzene with Metal Salts and Triethylamine in Methanol at Reflux



Entry	Metal Salt	Et ₃ N (equiv.)	Temp (°C)	Time (h)	MPc	Product	Yield (%)
1	Cu(OAc) ₂	5.0	65	24	CuPc	2a	39
2	Cu(OAc) ₂	10.0	65	24	CuPc	2a	27
3	Cu(OAc) ₂	3.0	65	24	CuPc	2a	31
4	Cu(OAc) ₂	0	65	72	CuPc	2a	0
5	Cu(OAc) ₂	Neat	89	48	CuPc	2a	0
6	Cu(OAc) ₂	5.0	78 ^a	48	CuPc	2a	21
7	Cu(OAc) ₂	5.0	rt	8 weeks	CuPc	2a	42
8	Cu(OAc) ₂	5.0	65	48	CuPc	2a	74
9	Cu(OAc) ₂	5.0	65	72	CuPc	2a	71
10	CuBr ₂	5.0	65	48	CuPc	2a	43
11	CuCl ₂	5.0	65	48	CuPc	2a	6
12	Cu(acac) ₂	5.0	65	48	CuPc	2a	9
13	Cu(NO ₃) ₂	5.0	65	48	CuPc	2a	36
14	CuSO ₄	5.0	65	48	CuPc	2a	35
15	CoCl ₂	5.0	65	48	CoPc	2b	27
16	Co(OAc) ₂	5.0	65	48	CoPc	2b	31
17	Zn(OAc) ₂	5.0	65	48	ZnPc	2c	38
18	Zn(NO ₃) ₂	5.0	65	48	ZnPc	2c	0
19	Ni(OAc) ₂	5.0	65	48	NiPc	2d	17
20	Ni(NO ₃) ₂	5.0	65	48	NiPc	2d	0
21	Mn(OAc) ₂	5.0	65	48	MnPc	2f	22
22	MnCl ₂	5.0	65	48	MnPc	2f	19
23	Mg(OAc) ₂	5.0	65	48	MgPc	2g	28

^a Ethanol at reflux instead of methanol

Table 2 Synthesis of Substituted Copper Phthalocyanines via Optimized Reaction Conditions

Entry	R ₁	R ₂	R ₃	Product	Yield (%)
1	H	H	H	2a	74
2	Cl	Cl	H	3	80
3	Me	H	H	4	57
4	<i>t</i> -Bu	H	H	5	69

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- [11] **Representative Procedure:** To a flame dried flask was added 1,2-dicyanobenzene (0.2288 g, 1.8 mmol, 1.0 equiv) in 20 mL of methanol. Then, the solution was degassed with argon for 10 minutes. Once the substrate was completely dissolved, a degassed solution of cobalt acetate (0.089 g, 0.45 mmol, 0.25 equiv) in 5 mL of methanol was added. Then the triethylamine (1.25 mL, 9.0 mmol, 5.0 equiv) was added. The resulting mixture was heated to reflux for 48 hours. The resulting deep blue-violet precipitate was filtered and washed with subsequent portions of methanol, water and then acetone until the filtrate was clear. Dried under reduced pressure afforded the cobalt phthalocyanine as a deep blue-violet solid, 0.0807 g (31% yield). HRMS (ESI) Calcd. for $C_{32}H_{16}N_8Co$: 572.0913. Found: 572.0903. Anal. Calcd. for $C_{32}H_{16}N_8Co$: C, 67.26; H, 2.82; N, 19.61. Found: C, 67.12, H, 2.97, N, 19.62. IR (neat): 1609, 1522, 1469, 1425, 1332, 1289, 1164, 1120, 1087, 913, 876, 780, 755, 732 cm^{-1} . All compounds synthesized here are known and in agreement with known spectral data.
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