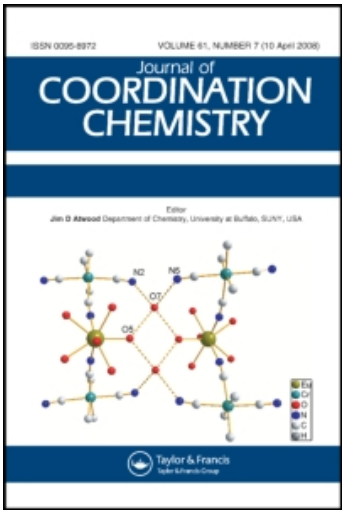

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A convenient synthesis of a substituted phthalocyanine compound

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A convenient synthesis of a substituted phthalocyanine compound

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A new substituted tetra-(4-octanethiol-5-nitro)phthalocyaninatocopper complex was synthesized by nucleophlic substitution of tetra-(4-bromo-5-nitro)phthalocyaninatocopper where the bromo activated by an *ortho*-nitro group is easily substituted by 1-octanethiol.

Keywords: Substituted phthalocyanine; Nucleophlic substitution

1. Introduction

Substituted phthalocyanines (Pcs) have received attention for their special physicochemical properties [1]. Usually, substituents are introduced to precursors such as phthalonitriles and then Pcs are obtained by condensation of the precursors. A precursor with specified substituents is not always readily available or, in other instances, hard to condense to Pc [2]. In this situation, introducing substituents to Pc directly instead of to the precursor is needed. However, direct substitution of the Pc ring often results in mixtures [3]. One method to reduce position indeterminacy is displacement of a group readily introduced to a precursor which is easy to condense to Pc.

Here we report the synthesis of tetra-(4-octanethiol-5-nitro)phthalocyaninatocopper using direct substitution of the bromo group on the Pc ring by 1-octanethiol (scheme 1). Although this substituted Pc can also be synthesized from a precursor bearing the octanethiol and nitro groups [4], the direct substitution method may be useful in syntheses of Pc where substituents are not stable in the condensation of precursor or the condensation is not qualitative.

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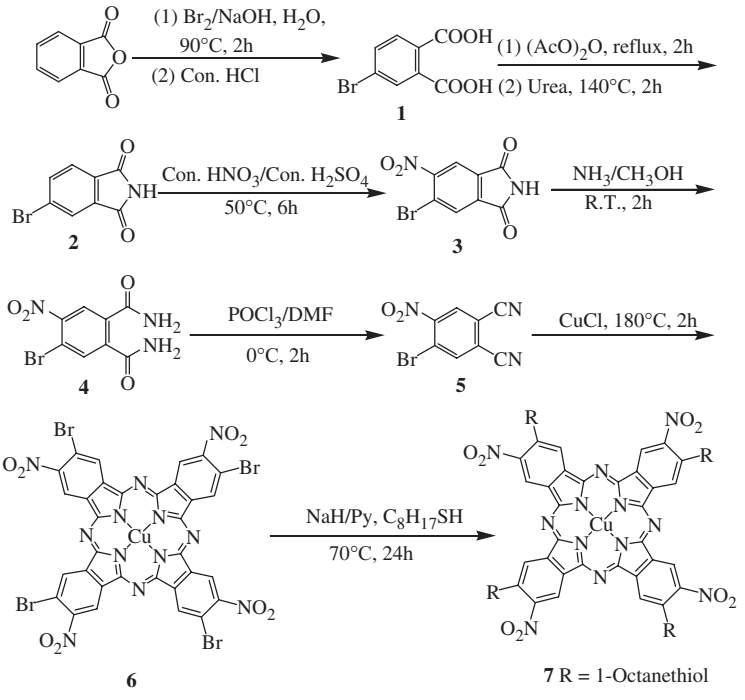

Scheme 1. Synthetic route to the title compound. Compounds **6** and **7** could have four structural isomers; scheme 1 shows one.

2. Experimental

2.1. *Physical measurements*

Melting points were measured on a WRS-1A melting point apparatus. Mass spectra were collected with a LCQ Deca XP MAX (ESI) mass spectrometer. Electronic absorption spectra were recorded on a Lambda-800 spectrophotometer and Elemental analyses were obtained with Vario EL III elemental analyses instrument. The crystal structure of **5** was determined on Rigaku RAXIS-RAPID (an X-ray imaging plate system) by using a graphite-monochromated Mo $K\alpha$ ($\lambda = 0.710688$ Å) radiation. All the reagents and solvents were of reagent grade and used without further purification.

2.2. *Synthesis*

2.2.1. Synthesis of compound 5. 4-bromophthalic acid (**1**) was prepared by bromination of phthalic anhydride according to the procedure described [5(a)] and obtained as a white crystalline powder in 61% yield, m.p. 166 ~ 167°C. 4-bromophthalimide (**2**) was prepared as a white crystalline powder by dehydration and imidization of **1** in 50% yield [5(d)], m.p. 230 ~ 233°C (lit. [5d]: 233–235°C). For nitration of **2** [5b–5d], 20.0 g (88 mmol) of 4-bromophthalimide and 32 mL of concentrated sulfuric acid were placed in a flask, and 4.4 mL of fuming nitric acid was added at 50°C with intense stirring. Reaction was continued for 6 h, and then the mixture was

poured into 500 mL ice water. The precipitate was filtered and washed by cold water until the filtrate was neutral then recrystallized from ethanol to give yellow powder, 4-bromo-5-nitrophthalimide (**3**) (10 g, yield 42%), m.p. 219 ~ 221°C (lit. [5d]: 216–218°C). 4-bromo-5-nitro- phthalamide (**4**) and 4-bromo-5-nitrophthalo-nitrile (**5**) were also prepared according to the procedure [5(b–d)]. Compound **4** was obtained by ammonolysis of **3** in methanol as a yellow powder in 94% yield, m.p. 214°C (decomposed, lit. [5d]: 216–218°C). Compound **4** reacted with $POCl_3$ in DMF to give the precursor **5** as a yellow crystalline powder in 70% yield, m.p. 158 ~ 159°C (lit. [5d]: 160–161°C). Crystallographic data of compound **5**: $C_8H_2BrN_3O_2$, $M = 252.03$, Orthorhombic space group $P2_12_12_1$ with a, 10.0191 Å; b, 6.8702 Å; c, 13.1706 Å; $V = 906.58$ Å^3 and $D_{Calcd} = 1.847$ g cm^{-3} for $Z = 4$. The structure was solved by direct methods (SHELXS-97, Sheldrick, 1990) and refined on F^2 using full-matrix least-squares techniques (SHELXL-97, Sheldrick, 1997) using 1210 data points to a R value of 0.2144 ($R_w = 0.4730$).

2.2.2. Synthesis of compound 6. A mixture of 4-bromo-5-nitrophthalonitrile (**5**) (0.51 g, 2.0 mmol) and CuCl (0.20 g, 2.0 mmol) was heated at 180°C under nitrogen for 2 h then cooled to room temperature and methanol (100 mL) was added. The precipitate was filtered and washed by methanol then dissolved in DMF and purified by chromatography (silica gel, DMF as eluent). Compound **6** was precipitated from the eluate by adding methanol; yield 60%. Anal. calcd for $C_{32}H_8Br_4CuN_{12}O_8$: C, 35.86; H, 0.75; N, 15.68%. Found: C, 36.43; H, 0.61; N, 15.13%. UV-Vis (λ_{max}, DMF): 683 nm.

2.2.3. Synthesis of compound 7. Under nitrogen and with intense stirring, 1-octanethiol (10 mL, 57 mmol) was slowly added to a mixture of sodium hydride (2.0 g, 83 mmol) and pyridine (20 mL) and the resulting mixture was stirred for 2 h at room temperature. Then the pyridine solution of compound **6** (0.27 g, 0.25 mmol) was added, and the mixture was stirred for further 24 h at 70°C. After cooling to room temperature, the solvent was removed by vacuum evaporation then crude product **7** was obtained as green solid. (MS (m/z): 1347.6, M^{2+} for **7** with a H_2O). The crude product was purified with chromatography (silica gel, $CHCl_3$ as eluent) then the final product was obtained after removing solvent by vacuum evaporation. Yield: 23%, MS (m/z): 1333.6 (M^+). Anal. Calcd for $C_{64}H_{76}CuN_{12}O_8S_4$: C, 57.66; H, 5.75; N, 12.61%. Found: C, 59.00; H, 6.01; N, 11.87%. UV-Vis (λ_{max}, DMF): 724 nm.

3. Results and discussion

The key intermediate 4-bromo-5-nitrophthalonitrile was synthesized as described in literature [5]. Bromination of phthalic anhydride in sodium hydroxide aqueous solution, followed by hydrolysis with concentrated hydrochloric acid gave **1** [5a]. Then compound **1** is dehydrated by acetic anhydride and reacted with urea to obtain **2** [5d]. The nitro group is introduced *via* a nitration reaction, followed by ammonolysis and dehydration by $POCl_3$ to yield the precursor **5** as a pale yellow solid [5b–5d]. Cyclotetramerisation of **5** with copper chloride at high temperature give tetra-(4-bromo-5-nitro)phthalocyaninatocopper (**6**). Then the title compound **7** was afforded by nucleophilic substitution with excess 1-octanethiol as a dark green solid.

The molecular structure of the dinitrile **5** was established by single-crystal X-ray diffraction analysis. Although the bad crystal quality of **5** resulted in a relative high *R* factor (0.2144), its molecular structure was accepted. As shown in figure 1, the bond length of C4–Br1 is 1.720(14) Å, which is much longer than that of C5–N3 (1.16(2) Å). It is also longer than the bond length of C–Cl (1.546 Å) of tetrachlorophthalonitrile [6a] and C–F (1.330 Å) of tetrafluorophthalonitrile [6b], which indicates that the bromo group of the compound **5** is a good leaving group compared with Cl and F in latter two phthalonitriles. By analogy, the bromo groups of compound **6** are supposed to be more easily nucleophilically substituted than the Cl and F in the $Cl_{16}Pc$ [7] and $F_{16}Pc$ [8] which reportedly led to polysubstituted products.

The MS analysis of crude final product **7** has proven that the tetra-(4-octanethiol-5-nitro)-phthalocyaninatocopper is the only one product of nucleophilic substitution (figure 2, $m/e = 1347.4$ for M^{2+} of $C_{64}H_{76}CuN_{12}O_8S_4 \cdot H_2O$). This is also confirmed

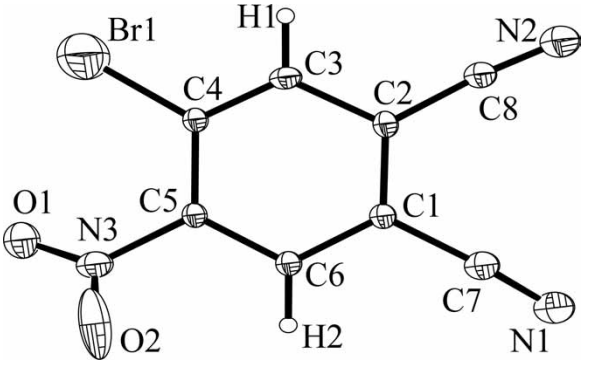

Figure 1. The molecular structure of **5** showing the atom labeling scheme.

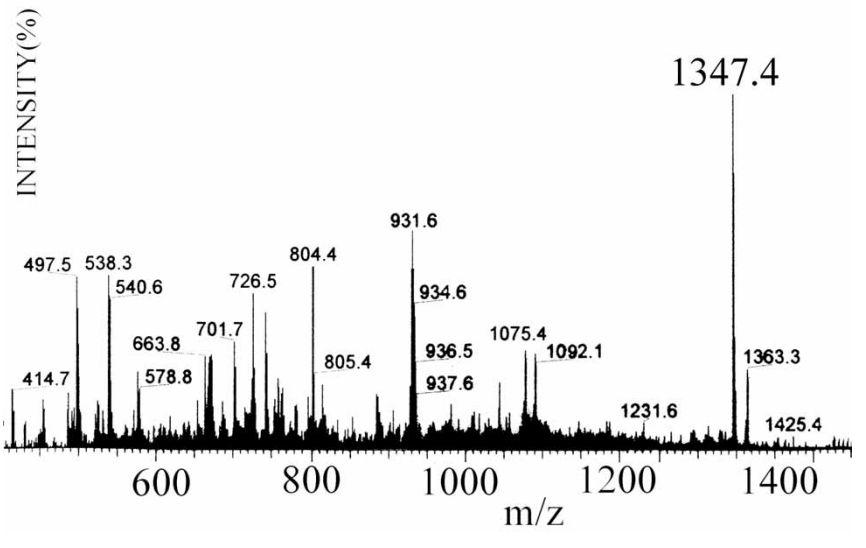

Figure 2. The mass spectrum of crude product of **7**.

by its solubility and UV-Vis spectra. Compound **6** is poorly soluble in most organic solvents, and sparingly soluble in DMF and Py. Compound **7** is soluble in most organic solvents. Moreover, the λ_{max} of Q band of **7** is 21 nm red shifted compared with **6**.

The fact that the substitution reaction is easy can be attributed to the effect of nitro group in lowering the electronic density of the C atom linked to the bromo atom. It is well known that the reaction rate of nucleophilic substitution of aromatic halides will be faster in the order of 10^2 to 10^3 times if they have ortho–nitro groups [9]. In addition, the yield of the substitution product also implied that there were not distinct steric effects of compound **6**.

4. Conclusion

In summary, 4-bromo-5-nitrophthalonitrile is easy to condense to Pc and the bromo group is readily substituted in a nucleophilic substitution reaction. This route may be useful in some syntheses of substituted Pc where the condensation reaction by the precursor bearing the target substitution group is difficult.

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