SYNTHESIS OF METALLOPHTHALOCYANINES UNDER SOLVENT-FREE CONDITIONS USING MICROWAVE IRRADIATION

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ABSTRACT: *Phthalocyanine complexes of Cu, Co, Ni, Fe, Zn, Pd, Pt and Ru have been synthesized from reaction between phthalonitrile and proper metal salts upon exposure to microwave irradiation under solvent-free conditions and considerably reduced reaction times.*

KEY WORDS: *phthalocyanine, metallophthalocyanine, phthalonitrile, microwave irradiation.*

Phthalocyanines are of interest not only as model compounds for the biologically important porphyrins but also because the intensely colored metal complexes are of commerical importance as dyes and pigments [1]. Preparation of metallophthalocyanines from the reaction between metal salts, particularly CuCl, phthalic anhydride and urea or phthalonitrile is carried out on a large scale industrially, the copper derivatives being an important blue pigment [2].

The Phthalonitrile process has the particular advantage over phthalic anhydride process of forming ring substituted chloro-metal phthalocyanines. A prerequisite for formation of the chloro substituted compounds however is the absence of ammonia or urea in the reactions [3].

Moreover, The Phthalonitrile process has the advantage of being the more elegant of the two syntheses. This technique makes it possible to produce metallophthalocyanines without obtaining substantial amounts of side products, a phenomenon which is understandable in view of the fact that the phthalonitrile molecule provides the parent structure of the phthalocyanine ring.

Typically, temperatures around 200°C and reaction times of hours are needed for preparation of metallophthalocyanines by the phthalonitrile process [4] (Scheme 1). It is not clear what the reducing reagent is in this process [5]. Long reaction times and high temperature produce mixtures of products from which the pure phthalocyanines may be difficult to obtain.

Microwave (MW) irradiation has been used to accelerate organic reactions, the efficient heating giving rise to remarkable rate enhancements [6,7].

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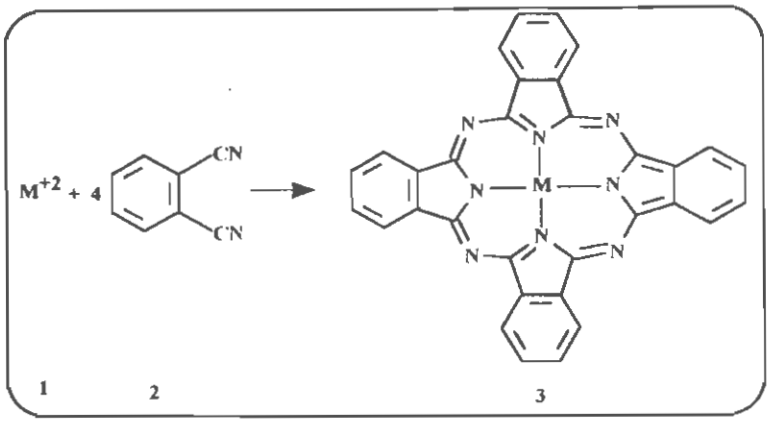

Scheme 1

Nevertheless, these procedures are seriously limited because use of solvents may lead to explosions.

In previous works [8], we have described a facile preparation of phthalocyanine complexes of Cu, Co, Ni, Fe, Ru, Pt, and Pd by using phthalic anhydride and urea in the absence of solvent. In this paper we report the preparation chlorine-free phthalocyanine complexes of Cu, Co, Ni, Fe, Zn, Pd, Pt and Ru by adding up to 20% urea in the phthalonitrile process. In this process not only pure products are obtained, but also no sublimation of raw materials occurs, whereas such difficulty exists in the phthalic anhydride and urea process.

The experimental procedure involves a simple mixing and grinding of reactants and irradiating mixture in a microwave oven for about 3 to 7 min in the absence of solvent. The reaction proceeds instantly as the melting of the mixture started after about 3 min. The results for various metallophthalocyanines are summarized in Table 1. Investigations toward extension of this procedure to other metals are in progress.

EXPERIMENTAL

Elemental analyses were performed using a Heraeus CHN-O rapid analyser. IR spectra were measured on a Shimadzu IR-470 spectrophotometer. Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operating at 70 eV. All starting materials were anhydrous. The IR spectra and fragmentation patterns of mass spectra of these compounds were in excellent agreement with those reported [9-15].

Table 1: Synthesis of metallophthalocyanines M(pc), using MW.

Entry	Product	Time/min	Yield(%)[a]
3a	[Cu(pc)]from CuCl	7	90(86)[b]
3b	[Co(pc)]from $CoCl_2$	6	85(80)
3c	[Ni(pc)] from $NiCl_2$	5.5	85(80)
3d	[Fe(pc)] from $FeCl_2$	3	91(86)
3e	[Zn(pc)] from $ZnCl_2$	4	87(80)
3f	[Pd(pc)] from $PdCl_2$	6.5	68(50)
3g	[Pt(pc)] from $PtCl_2$	6	81(65)
3h	[Ru(pc) from $RuCl_3$	5.5	76(60)

a) Based on the phthalonitrile

b) After Soxhlet extraction

The preparation of copper phthalocyanines is representative of the general procedure employed for Co, Ni, Fe and Zn.

The phthalonitrile (0.98 g, 7.65 mmol), urea (0.20 g, 3.33 mmol), copper (I) chloride (0.19 g, 1.92 mmol), and sodium sulfate (2.00 g, 14.08 mmol), were ground together until homogeneous, then placed in an beaker and irradiated in a microwave oven at high power for 7 min. Upon completion of the reaction, the product was ground and washed with hot water and methanol respectively. The dried phthalocyanines thus obtained weighed 1.0 g, (yield 90% based on phthalonitrile. [Cu(pc)] was subsequently recrystallized two times from concentrated H_2SO_4. For recrystallization, the solution of phthalocyanine

in concentrated H_2SO_4 was poured into distilled water [16]. After recrystallization, the [Cu(pc)] obtained was purified by Soxhlet extraction. Using methanol and methylene chloride and purified further by two times vacuum sublimations. (Found: C, 66.7; H, 2.5; N, 19.2; Cu, 11.0. Calc. for $C_{32}H_{16}N_8$-Cu: C, 66.74; H, 2.78; N, 19.45; Cu, 11.03). ν_{max}(KBr)/cm^{-1}, 731, 755, 779, 874, 893, 1083, 1115, 1158, 1275, 1325, 1408, 1451, 1493, 1597. MS: m/z(%) 575(56, M^+), 288(17, M^{+2}), 191(17, M^{+3}), 128(13, $C_6H_4(CN)_2$), 63(26, Cu^+), 44 (100).

[Co(pc)] (Found: C, 67.3; H, 2.7; N, 19.5; Co, 10.1. Calc. for $C_{32}H_{16}N_8$-Co: C, 67.28; H, 2.80; N, 19.61; Co, 10.32). ν_{max}(KBr)/cm^{-1}, 728, 756, 777, 862, 910, 1087, 1117, 1159, 1280, 1328, 1422, 1458, 1525, 1599. MS: m/z(%) 571(100, M^+), 286(36, M^{+2}), 187 (27, M^{+3}), 128(18, $C_6H_4(CN)_2$), 59(45, Co^+), 44(18).

[Ni(pc)] (Found: C, 67.1; H, 2.7; N, 19.5; Ni, 10.2. Calc. for $C_{32}H_{16}N_8$-Ni: C, 67.30; H, 2.80; N, 19.61; Ni 10.28). ν_{max}(KBr)/cm^{-1} 733, 756, 780, 869, 900, 1090, 1117, 1158, 1279, 1327, 1414, 1457, 1511, 1599. MS: m/z(%) 570(100, M^+), 285(39, M^{+2}), 186(26, M^{+3}), 128(17, $C_6H_4(CN)_2$), 58(43, Ni^+), 44(10).

[Fe(pc)] (Found: C, 67.6; H, 2.8; N, 19.8; Fe 9.8. Calc. for $C_{32}H_{16}N_8$-Fe: C, 67.64; H, 2.82; N, 19.71; Fe, 9.83). ν_{max}(KBr)/cm^{-1}, 731, 756, 779, 867, 904, 1079, 1116, 1157, 1279, 1327, 1412, 1461, 1502, 1602. MS: m/z(%) 568(100, M^+), 284(29, M^{+2}), 128(7, $C_6H_4(CN)_2$), 56(29, Fe^+), 44(39).

[Zn(pc)] (Found: C, 66.2; H, 2.5; N, 19.4; Zn, 11.0. Calc. for $C_{32}H_{16}N_8$-Zn: C, 66.53; H, 2.77; N, 19.39; Zn, 11.32). ν_{max}(KBr)/cm^{-1}, 723, 749, 771, 881, 945, 1052, 1080, 1114, 1157, 1275, 1325, 1400, 1436, 1475, 15.96. MS: m/z(%) 576(100, M^+), 288(45, M^{+2}), 192(14. M^{+3}), 128(36, $C_6H_4(CN)_2$), 64(54, Zn^+), 44 (100).

The preparation of palladium phthalocyanines is representative of the general procedure employed for Pt and Ru.

The phthalonitril (1.54 g, 12 mmol), urea (3.70 g, 61 mmol), ammonium chloride (0.60 g, 11.3 mmol), ammonium molibdate (0.0033 g, 2.80×10^{-3} mmol as catalyst) and palladium chloride (0.07 g, 0.4 mmol) were ground finely. The ground materials were placed in a beaker and irradiated in the microwave oven at high power for 5 minutes. When the reaction was started the power turned to medium and irradiated until the reaction completed (1.5 min.). The product was ground and washed with 200 mL of hot water and dried. The crude PdPc subsequently was reprecipitated three times from concentrated H_2SO_4, (0.17 g, yield 68%). PdPc was further purified by 3 hours Soxhlet extraction with acetone [10] and two times vacuum sublimations. (Found: C, 61.5; H, 2.6; N, 17.9. Calc. for $C_{32}H_{16}N_8$-Pd; C, 62.09; H, 2.60; N, 18.10). ν_{max}(KBr)/cm^{-1}, 726, 758, 765, 807, 863, 906, 938, 997, 1062, 1101, 1116, 1159, 1275, 1310, 1347, 1406, 1467, 1493, 1599. MS: m/z(%) 618(78. M^+), 128(26, $C_6H_4(CN)_2$), 44(100).

[Pt(pc)] (Found: C, 53.5; H, 2.3; N, 16.2. Calc. for $C_{32}H_{16}N_8$-Pt: C, 54.31; H, 2.28; N, 15.84): ν_{max}(KBr)/cm^{-1}, 729, 765, 772, 911, 941, 998, 1064, 1114, 1159, 1279, 1318, 1368, 1410, 1453, 1598, 1599. MS: m/z(%) 708(95, M^+), 128(43, $C_6H_4(CN)_2$), 44(100).

In the case of [Ru(pc)], dehydrated $RuCl_3$ was used and for purification of crude product we employed Soxhelt extraction with pyridine until the solvent was colorless (10 h, yield 76%). The obtained $PcRu(py)_2$ was further purified by column chromatography (neutral alumina, $CHCl_3$) [11] (yield 60%). (Found: C, 64.5; H, 2.3; N, 18.5. Calc. for $C_{42}H_{26}N_{10}$- Ru: C, 65.35; H, 3.39; N, 18.15): ν_{max}(KBr)/cm^{-1}, 730, 756, 776, 866, 906, 935, 998, 1061, 1119, 1164, 1281, 1318, 1408, 1434, 1485, 3040. MS: m/z(%) 385(10, M^{+2}), 128(100, $C_6H_4(CN)_2$), 44(57).

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