# Notes

## Complexes derived from Phthalonitrile. The Intermediates to Nickel Phthalocyaninate

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The formation of [Ni(pc)] (pc = phthalocyaninate) through the stepwise reactions of nickel ion and phthalonitrile in a two-compartment electrolyzer separated with an ion-exchange membrane is traced. Five reaction intermediates, which readily convert to [Ni(pc)] upon heating, were isolated by means of preparative thin-layer chromatography and characterised mass spectrometrically.

Recently we demonstrated a novel synthetic route towards a metal phthalonitrile employing a two-compartment electrolytic cell separated by an ion-exchange membrane under ambient conditions.[1] The formation of the metal phthalocyaninate could thus be traced through the various intermediates, which had previously eluded detection in the conventional template reactions at relatively high temperature.

### Experimental

*Materials.*—All chemicals employed were standard reagents and used without further purification.

*Pretreatment.*—The construction and operation of the electrolytic cell is the same as described elsewhere.[1] A total of 100 mol dm$^{-3}$ of an ethanolic solution containing tetrabutylammonium perchlorate (0.02 mol dm$^{-3}$) and phthalonitrile (0.02 mol dm$^{-3}$) was placed in the cathode compartment, whereas 100 mol dm$^{-3}$ of an ethanolic solution of nickel sulphate served as anolyte. The electrolysis was carried out at $-1.6$ V *versus* s.c.e. and 60—100 mA for 3 h at room temperature.

The catholyte was filtered and the formed [Ni(pc)] together with other insolubles were removed. The filtrate was solvent extracted with carbon tetrachloride. A red solid was obtained after the solvent was pumped off, which was then dissolved in acetone for the subsequent chromatographic separations.

*Preparation of Thin-layer Chromatography Plate.*—Silica gel (17 g) (Merck 7 747) was immersed in 7.5% $Na_2CO_3$ solution (50 cm$^3$) and then dispersed on a 20 × 20 cm glass plate. The plate was air dried and activated in an oven at 110 °C for 3 h before use.

*Separation and Characterization of the Intermediates.*—The acetone solution of the red solid was spotted on a t.l.c. plate and developed with a chloroform–benzene (1 : 5) solution for 2 h. A red band at $R_f = 0.7$ (A) and a continuum (B) down to the origin were obtained. The latter was removed from the plate, extracted with acetone, and then subjected to a second development on another fresh plate using a chloroform–ethyl acetate (10 : 1) mixture. Distinct bands at $R_f$ = 0.8, 0.7 (C), 0.28 (D), 0.15 (E), and 0.1 (F) were obtained. Except for $R_f = 0.8$, all the other intermediates turned into [Ni(pc)] gradually at room temperature and rapidly upon heating. However, they could be stored at 0 °C for a few days without appreciable change.

Since the intermediates underwent deterioration in the course of sample preparation and measurement, no reproducible i.r. spectra could be obtained. The characterization was therefore performed mainly on a JOEL-JMS-D-100 mass spectrometer. The characteristic fragmentation ions together with their assignments are given in the Table. The remarkably abundant ion at *m/e* = 588 might be more thermally stable than its precursors.

*Separation and Characterization of the By-products.*—After electrolysis, the catholyte was drawn out and heated above 60 °C for several hours to ensure the formation of [Ni(pc)]. The precipitate was filtered off and purified for the [Ni(pc)] as described previously.[1] The red filtrate was treated with water to obtain a precipitate, which was filtered off and subjected to a two-step sublimation between 70—120 and 180—200 °C, respectively. The white and red sublimates were characterized as phthalimide and 2,4,6-tri(*o*-cyanophenyl)-1,3,5-triazine, a trimer of phthalonitrile, respectively.

A solid was obtained upon concentration of the filtrate, which was recrystallised and characterised as 3-imino-

**Table.** Mass spectral data of the intermediates [a]

| Intermediates | Characteristic fragmentation ions (*m/e*) [b] |
|---|---|
| (A) | 634 (27.8, $C_{34}H_{24}N_8NiO_2^+$), 588 (100), 570 (4.2), 562 (14.0), 556 (4.2) |
| (C) | 698 (17.3, $C_{36}H_{32}N_8NiO_4^+$), 634 (55.3), 588 (100), 570 (22.7), 562 (2.62), 556 (9.3) |
| (D) | 744 (2.7, ?) [c]<br>678 (5.5), 635 (41.6), 632 (51.4), 588 (100), 570 (2.2), 562 (4.1), 556 (5.5) |
| (E) | 680 (8.7, $C_{36}H_{30}N_8NiO_3^+$), 634 (43.4), 588 (100), 570 (86.9), 562 (13), 556 (26.2) |
| (F) | 724 (2.2, $C_{38}H_{34}N_8NiO_4^+$), 678 (4.4), 634 (40), 588 (100), 570 (31.1), 562 (7), 556 (15.5) |

[a] The intermediates separated from ethanol solution. [b] Both relative intensities and assignments are included in parentheses. Except for $^{58}$Ni, all other isotopic ions are neglected. [c] A meaningful ion molecule cannot be assigned readily, however, fragments derived therefrom are also found in other intermediates.

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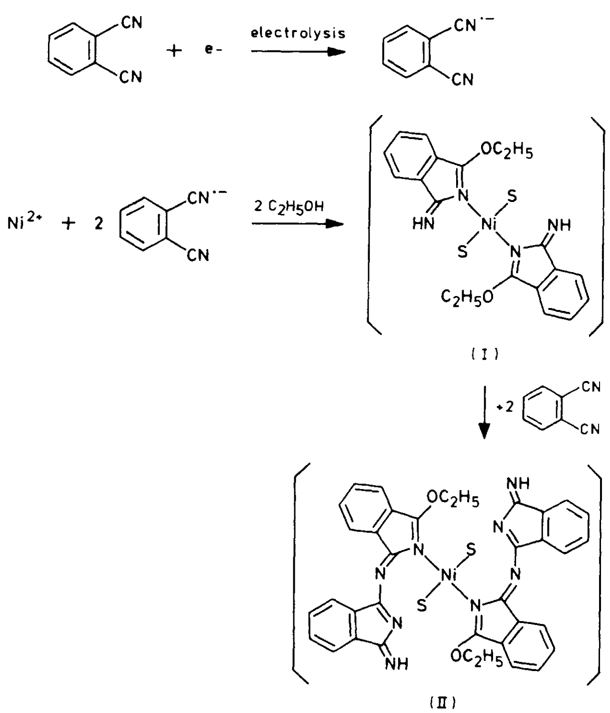


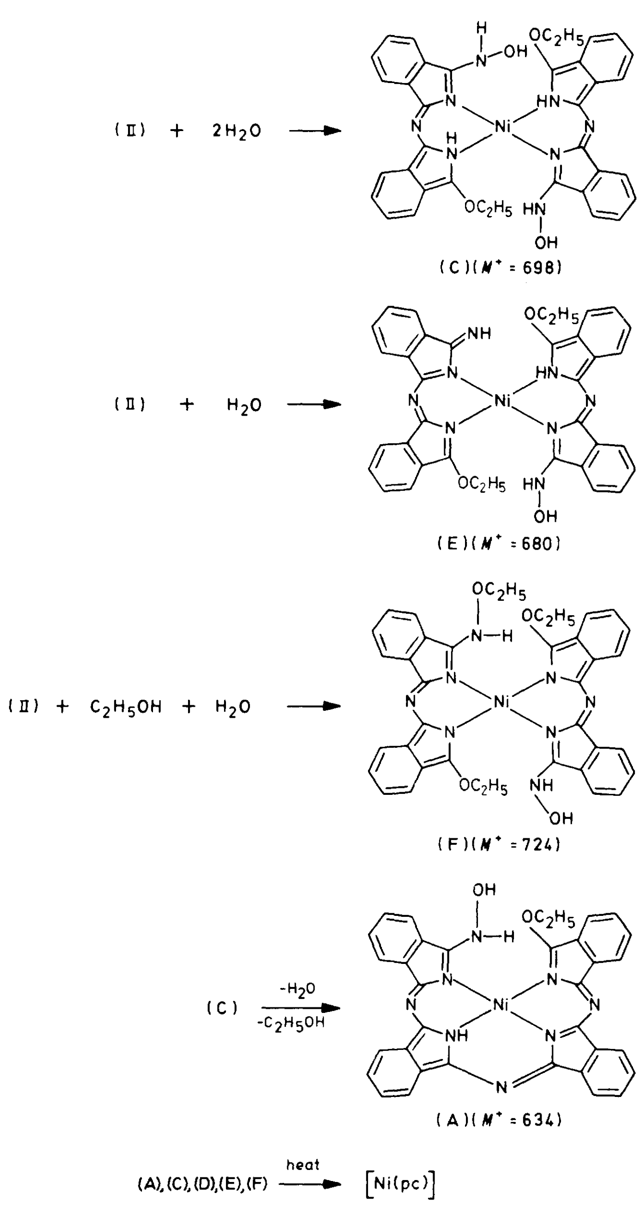
**Scheme 1.** S = Solvent

phthalimidine. The i.r. and $^1$H n.m.r. spectra of these by-products are all in agreement with published data.[2]

## Discussion

It has been shown in a previous paper [1] that the phthalonitrile anion radicals generated at the cathode play an important role in the cyclization leading to the formation of the metal phthalocyaninate.[2] Moreover, it has been noted that the solvent molecules might actively participate in the reaction, since the formation of the metal phthalocyaninate was observed in the presence of an appropriate protic solvent such as alcohols and *NN*-dimethylformamide, but not in acetonitrile, although the anion radicals could be generated in this medium.

By careful operation, we were able to isolate several of the intermediates to the formation of [Ni(pc)]. The intermediates (I) and (II) are not isolable (see Scheme 1) however, but the reactions derived therefrom as shown in Scheme 2 seem to be plausible. The other intermediates which are brought forth by the subsequent reactions of (II) with solvent molecules are also conceivable, since an analogue of (E) containing a pentoxy group has been synthesised and characterized,[3] which probably owes its stability to the bulkiness of the pentoxy group. Heating of the intermediates results in the splitting off of the alkoxy group and the rearrangement of bonds involving ring closure in the formation of [Ni(pc)]. The fact that an electrolysis conducted in an absolute alcoholic medium gives a higher yield of [Ni(pc)] together with very few by-products and intermediates can readily be visualized in the light of the Schemes.



**Scheme 2**

## Acknowledgements

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## References

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