Charge Transfer Complexes of Phthalocyanine

by

H. Nakai and M. Isutsui

Texas A&M University
Department of Chemistry
College Station, Texas 77843

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H. Nakai and M. Tsutsui

Department of Chemistry
Texas A&M University
College Station, Texas 77843

Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

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The attempts of the preparation from alkyl derivatives of tetrazoporphine and octaazaphthalocyanine and hexadecafluorophthalocyanine are reported.
I. Introduction

Our laboratory has been engaged in the study of the synthesis of a new type of metallo-organic polymer using metalloporphyrins. In the past decade a new chemistry has been developed in this area, and we have successfully synthesized a promising monomeric skewed complex.\textsuperscript{1-4} Metallo-organic polymers have the potential to be one dimensional conductors with metal-like conductivity.\textsuperscript{5} The best one dimensional conductors known so far are those with equivalent molecules in stacks.\textsuperscript{6} These compounds are formed from d\textsuperscript{8} metal square planar complexes with small planar ligands. Interestingly enough, porphyrin ligands could fit some of the criteria for good design of a one dimensional ligand. In this context our efforts have been directed toward the preparation of a new type of metallo-organic polymer using the skewed complex and other monomeric metalloporphyrin complexes, and we have investigated other macrocyclic ligands, such as phthalocyanines and tetraaza[14]annulenes.

Among the ligands mentioned above, emphasis was placed on the chemistry of organometallophthalocyanines in our laboratory. Metallophthalocyanines\textsuperscript{7} are known to exhibit semiconductivity, photoconductivity, photovoltaic effect, flocculation tendency, and extraordinary thermal stability. These properties are expected to contribute to give the desirable properties, particularly metal-like electrical conductivity, in our one dimensional metallophthalocyanine polymer. If octa-coordinate metal ions could coordinate
to two phthalocyanine ligands in a manner similar to tin (IV) bis(phthalo-
cyanine), and if a polymer or a charge transfer complex could be formed from 
this unit complex, a metal-metal bond might pass through the center of the 
phthalocyanine or analogous ligand core. This aligning of metal centers 
into a one dimensional structure may enhance the electronic conductance 
of such a polymer or charge transfer complex. Phthalocyanine complexes of 
lanthanide metal ions, [MPC]₂H, and bis(phthalocyanine) tin (IV) have been 
postulated to possess a sandwich type structure. Recently, the structures 
of bis(phthalocyanine) uranium (IV) and bis(phthalocyanine) tin (IV) have 
been determined by x-ray diffraction studies. In these complexes the two 
phthalocyanine ring systems form a sandwich-type structure with the metal 
atom in the center. The uranium (IV) complex is a significant compound in 
the study of possible f-orbital participation in coordinative bonding. 
However, the uranium complex is moisture sensitive and practical use of 
the complex is dubious, but the tin complex is stable toward both air and 
moeisture and like the mercury complex may possess potential use in the 
formation of polymers.

Metalloporphyrins are reported to form charge transfer complexes with 
strong electron acceptors such as Ni(S₂C₂(CF₃)₂)₂(Ni(tfcd)₂), trini-
troarenes, tetracyanoethylene, and tetracyanoquinodimethane. Copper 
phthalocyanine polymer has the highest mobility, a parameter of electronic 
conductivity, of any organometallic compound. One difficulty of phthalo-
cyanine chemistry is its insolubility towards organic solvents. This pre-
sents a serious problem in the synthesis of desired compounds. To overcome 
this problem and to prepare a one dimensional polymer, the preparation of 
an electron donor-acceptor complex from two kinds of phthalocyanine or 
phthalocyanine-type molecules appears to be a possible mode of attack.
In this case a phthalocyanine with more electron donor character and the other phthalocyanine with strong electron acceptor character could be reacted. Examples of the former type of phthalocyanine are alkyl derivatives of tetraazaporphine and octaazaphthalocyanine, and an example of the latter is hexadecafluorophthalocyanine (see Figure 1).

Phthalocyanines are known to function as both electron donor and acceptors. Therefore the combination of a metallophthalocyanine with an electron donating group and a metallophthalocyanine with a strong electron accepting character might form the desired one dimensional polymer with metal-like conductivity.

We have studied the synthesis of monomer unit complexes of organo-metallophthalocyanines with strong electron donor or acceptor characters. Some of the former compounds are metallotetraazaporphines, metalloctaazaphthalocyanines, etc., and the latter metallophthalocyanines, metallo-hexadecafluorophthalocyanines, etc.

We have further attempted to prepare charge transfer complexes from a combination of metallophthalocyanine or phthalocyanine type compounds with strong donor and acceptor characters.

II. Results and Discussions

Phthalocyanines and their analogues are known to function as donors and to form charge transfer complexes with acceptors. Tetracyano-p-quinodimethane (TCNQ) forms highly conducting radical anion complexes. The TCNQ complexes have been reported to contain one dimensional conducting chains of face-to-face stacked TCNQ units. Reported conductivity and magnetic data suggest that these complexes form "columns" or radical cationic and anionic units. When dilithiumphthalocyanine was used as donor and reacted with TCNQ in acetone or ethanol solution at ambient temperature, an
a. Metallotetraazaporphines
b. Metallooctaaazaphthalocyanines
c. Metallohexadecafluorophthalocyanines
Immediate color change was observed. The precipitate which formed was separated and investigated by spectroscopy. The product is soluble in neither acetone nor ethanol, and its visible spectrum indicates that it was most likely free phthalocyanine. If the product was a dilithium phthalocyanine–TCNQ complex, the visible spectrum should be similar to a combination of the spectra of dilithium phthalocyanine and TCNQ. Apparently TCNQ reacted with lithium ion of dilithium phthalocyanine in these solvents and formed Li⁺TCNQ⁻ and free phthalocyanine instead of the desired complex or polymer.

If one can find a suitable solvent for this reaction, the result may differ. Dilithium phthalocyanine is not suitable for synthesis of a phthalocyanine–TCNQ complex in common organic solvents. Phthalocyanines with more electron donating character than dilithium phthalocyanine and with non-reactive metals towards TCNQ should be used for this purpose.

In order to obtain metallophthalocyanines with more electron donating character than phthalocyanine itself, a number of known phthalocyanine derivatives appeared to be most electron rich and therefore might be a donating phthalocyanine derivative. Alkyl derivatives of tetrapyrazinoporphyrazine were expected to have better solubility. The synthesis and use of octamethyl-tetrapyrazinoporphyrazine were therefore studied.

When 2,6-dicyano-5,6-dimethylpyrazine was heated with magnesium or zinc metal at 200°C a reaction took place, and a brown-black solid was formed. The product was expected to be a metal tetra-4,5-dimethyloctaaza porphin. However, the product was not soluble in any organic solvents. When the product was dissolved in conc. H₂SO₄, recovery of the products was not possible. Attempted purification of the product by sublimation failed to give any product because the compound did not sublime even at 500°C. Extraction of the crude product with either pyridine or dimethylformamide gave some solid
product which was not soluble in cold pyridine or dimethylformamide and was not identified.

Since ruthenium carbonyl phthalocyanine is known to be soluble to various organic solvents, an attempt was made to prepare ruthenium octamethyltetrapyrazinoporphyrizine from reaction of ruthenium trichloride with 2,3-dicyano-5,6-dimethylpyrazine. Although the product has a dark blue color with purple luster which is typical of metallophthalocyanines, it was, unfortunately, totally insoluble in any organic solvents tested. The product also showed low solubility in concentrated sulfuric acid. Since this insoluble property presents a serious problem for future use of these complexes as the starting materials for preparation of charge transfer complexes, the investigation of these compounds was suspended.

Although phthalocyanines are reported to be electron acceptors, their poor solubility towards organic solvents prevents their useful application in the synthesis of charge transfer complexes. Perfluorophthalocyanines have more electron accepting character than phthalocyanines and are known to be soluble to ketones. Moreover, tetrafluorophthalonitrile is commercially available for the preparation of metal perfluorophthalocyanines. Zinc hexadecafluorophthalocyanine was obtained from the reaction of tetrafluorophthalonitrile with zinc dust in boiling α-chloronaphthalene. The resulting purple crystals, which yield a bright blue powder when crushed, were presumed to be analogous to the product formed by a similar treatment of phthalonitrile. Zinc hexadecafluorophthalocyanine is very thermally stable and can be purified by sublimation. Zinc hexadecafluorophthalocyanine is soluble in α-chloronaphthalene and ketones giving blue solutions. Therefore, chromatographic purification can be applied to this type of phthalocyanine compound. As with the majority of phthalocyanine compounds, perfluorophthalocyanine is also soluble in concentrated
sulfuric acid and may be precipitated by the addition of water.

The reaction of tetrafluorophthalonitrile with the theoretical quantity of magnesium powder in α-chloronaphthalene yielded a kakhi colored product. The color and the visible spectrum of the product indicated that it was very unlikely to be magnesiumhexadecafluorophthalocyanine.

No further attempt to prepare charge transfer complexes has been made because no suitable phthalocyanine derivatives with electron donor character have been synthesized at this time.

III. Experimental

Charge Transfer Complexes of Phthalocyanines

The Reaction of Dilithium Phthalocyanine with Tetracyanoquinodimethane (TCNQ)

Attempt 1. To a greenish yellow solution of TCNQ (0.009 g) in acetone, a blue solution of dilithium phthalocyanine in acetone was added at room temperature. Immediately the color of the reaction mixture turned dark brown. After standing for 40 minutes, a brown solid was isolated by filtration, washed three times with 10 mL of n-pentane, and dried in a desiccator. The visible spectrum of the product in chloronaphthalene was identical to that of free phthalocyanine.

Attempt 2. To a greenish yellow solution of TCNQ (0.044 g) in absolute ethanol a blue solution of dilithium phthalocyanine in ethanol was added at 50°C. Immediately the color of the reaction mixture turned greenish blue. After cooling to room temperature, the resulting blue solid was isolated by filtration, was washed three times with 10 mL of n-pentane, and dried in a desiccator.
The visible spectrum of the product indicates that it was a mixture of monolithium phthalocyanine and free phthalocyanine.

**Preparation of Metallophthalocyanines with Electron Donor Character**

**The Reaction of Ruthenium Trichloride with Dilithium Phthalocyanine**

Dilithium phthalocyanine (0.79 g) and ruthenium trichloride (0.50 g) were allowed to reflux for 20 minutes in dimethylformamide. After being cooled to room temperature, the resulting precipitate was isolated by filtration, washed with benzene and hexane, and dried in a desiccator. After several trials, it was found that the product was most likely free phthalocyanine according to its infrared and visible spectra.

**Ruthenium Phthalocyanine**

Phthalonitrile (1.55 g) was heated to reflux with an excess of ruthenium for 5 hours. The blue solid which slowly formed was ground into powder form, washed three times with 20 mL of methanol, and extracted with acetone for 24 hours. The blue acetone extract was evaporated down to 10 mL and added to n-pentane. The resulting precipitate was isolated by filtration and dried in a desiccator. This fraction was never identified. The acetone insoluble residue was extracted with aniline for 20 hours. The blue aniline extract was evaporated down to 5 mL and added to acetonitrile. The resulting precipitate was isolated by filtration and dried in a desiccator. This product should be dianiline ruthenium phthalocyanine.

**Magnesium Octamethyltetrapyrazinoporphyrizine**

**Attempt 1.** 2,3-Dicyano-5,6-dimethylpyrazine (1.3 g) was heated with an excess of etched magnesium at 200°C for 30 minutes under argon. The color of
the reaction mass rapidly turned blue then brownish black. The cooled reaction mass was ground into a fine powder and treated with a dilute hydrochloric acid solution to remove any unreacted magnesium. The resulting powder was washed with water, ethanol, and acetone, and then was extracted with 2-pentanone for 120 hours and with dimethylformamide for 24 hours. Removal of the solvent from the above two extracts yielded trace amounts of products which were unidentified. The residue was not very soluble even in concentrated sulfuric acid.

**Attempt 2.** The experiment above was repeated open to the air, and a similar result was obtained (more carbon black was formed).

**Attempt 3.** 2,3-Dicyano-5,6-dimethylpyrazine (0.80 g) was heated with an excess of magnesium chloride at 200° for one hour under argon. The color of the reaction mass gradually turned green and dark blue. The reaction mass was treated as in the previous attempts. Extraction with dimethylformamide did not yield any solid product, indicating that the product was decomposed in boiling dimethylformamide.

**Zinc Octamethyltetrapyrazinoporphyrazine**

**Attempt 1.** 2,3-Dicyano-5,6-dimethylpyrazine (1.0 g) was heated with an excess of etched zinc at 200° for 30 minutes under argon. The cooled reaction mass was ground into a fine powder and treated with a dilute hydrochloric acid solution to remove any unreacted zinc. The product was not very soluble to concentrated sulfuric acid or any organic solvents.

**Attempt 2.** 2,3-Dicyano-5,6-dimethylpyrazine (0.82 g) was heated with an excess of zinc chloride at 200°C for one and one-half hour under argon. The
color of the reaction mass turned dark green then dark blue. The cooled reaction mass was ground into a fine powder, washed with water, ethanol, and acetone and dried in a desiccator. Extraction with dimethylformamide yielded a black solid which was discarded. Extraction with pyridine and subsequent removal of solvent under reduced pressure yielded a dark green solid.

Ruthenium Octamethyltetrapyrazinoporphyrazine

2,3-Dicyano-5,6-dimethylpyrazine (1.2 g) was heated with an excess of ruthenium trichloride at 235° for 5 minutes. The dark brown color of the reaction mass suddenly turned dark purple at 235°. The cooled reaction mass was ground into a fine powder, washed with water, ethanol and acetone, and dried in a desiccator. The product was not soluble in any organic solvent tested and slightly soluble in conc. H₂SO₄.

Preparation of Metallophthalocyanines with Electron Acceptor Character

The Reaction of Magnesium with Tetrafluorophthalonitrile

Magnesium metal powder (0.66 g) and tetrafluorophthalonitrile (1.0 g) were allowed to reflux in 1-chloronaphthalene for 96 hours under argon. Initially the dark green color gradually turned brown. After cooling to room temperature the reaction mixture was diluted with n-hexane. The kakhi colored precipitate which formed was isolated by filtration, washed twice with 20 mL of ethanol, twice with 20 mL of n-hexane, and dried in a desiccator. The infrared and visible spectra of the product were different from those of the reported metalloperfluorophthalocyanines. Moreover all reported metalloperfluorophthalocyanines have blue or purple color. Therefore further investigation of the product was not carried out.
The Reaction of Zinc with Tetrafluorophthalonitrile

Zinc metal powder (1.4 g) and tetrafluorophthalonitrile (2.0 g) was allowed to reflux in 1-chloronaphthalene for 50 hours under argon. Initially the light yellow color gradually turned dark brown. The resulting black solid was isolated by filtration and was treated with dilute hydrochloric acid to remove any unreacted zinc. The product was then washed with absolute ethanol and n-hexane. The resulting residue was extracted with refluxing 2-pentanone for 48 hours. Removal of solvent from the extract yielded a dark blue solid which was identified as zinc perfluorophthalocyanine from its infrared and visible spectra.

Rutheniumcarbonylperfluorophthalocyanine

Ruthenium dodecacarbonyl (0.22 g) and tetrafluorophthalonitrile were allowed to reflux in diphenylmethane (40 g) for 24 hours under argon. Initially the light orange color gradually turned dark blue. The reaction mixture was concentrated into 5 mL by removal of solvent under vacuum and was allowed to cool to room temperature. The resulting purplish blue solid was isolated by filtration, washed twice with 20 mL of hexane, and dried in a desiccator. Thin layer chromatography of the product indicated that it was a pure compound.

The Reaction of Chromium Hexacarbonyl with Tetrafluorophthalonitrile

Chromium hexacarbonyl (0.15 g) and tetrafluorophthalonitrile (0.55 g) were allowed to reflux in diphenylmethane for 24 hours under argon. The product which formed was isolated as in the preparation of rutheniumcarbonyl-perfluorophthalocyanine. TLC showed that the product was not chromium-perfluorophthalocyanine.

The Reaction of Molybdenum Hexacarbonyl with Tetrafluorophthalonitrile
Molybdenum hexacarbonyl (0.29 g) and tetrafluorophthalonitrile (0.74 g) were allowed to reflux in diphenylmethane for 24 hours under argon. The product which formed was treated in a similar manner. TLC showed that the product was not molybdenum-perfluorophthalocyanine.

The Reaction of Tungsten Hexacarbonyl with Tetrafluorophthalonitrile
Tungsten hexacarbonyl (0.23 g) and tetrafluorophthalonitrile (0.59 g) were allowed to reflux in diphenylmethane for 26 hours under argon. The product which formed was treated in a similar manner. No phthalocyanine product was formed according to the TLC test.

The Reaction of Dirhenium Decacarbonyl with Tetrafluorophthalocyanine
Dirhenium decacarbonyl (0.25 g) and tetrafluorophthalonitrile (0.50 g) were allowed to reflux in diphenylmethane for 24 hours in an argon atmosphere. The product which formed was treated in a similar manner. No phthalocyanine product was formed according to the TLC test.

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