AD-A060 571 TEXAS A AND M UNIV COLLEGE STATION DEPT OF CHEMISTRY F/G 7/3
CHARGE TRANSFER COMPLEXES OF PHTHALOCYANINE.(U)
OCT 78 H NAKAI, M TSUTSUI N00014-75-C-0417
UNCLASSIFIED TR-26 NL

| OF |

AD
A060571

END
DATE
FILMED
01-79
DDC

(12) LEVEL II

NW

AD A060571

OFFICE OF NAVAL RESEARCH

(15) Contract N00014-75-C-0417
Task No. NR 053-559

(14) TR-
Technical Report No. 26

(9) Interim rept.

(6)
# Charge Transfer Complexes of Phthalocyanine,

by

(10)
H. Nakai [redacted] M. Tsutsui

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

DDC FILE COPY

DDC
RECEIVED
NOV 1 1978
B

(11) 15 Oct[redacted]78

(12) 19p.

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited.

78 10 23 113

407 997

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

## REPORT DOCUMENTATION PAGE

**READ INSTRUCTIONS BEFORE COMPLETING FORM**

1. REPORT NUMBER
Technical Report No. 26

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (*and Subtitle*)
Charge Transfer Complexes of Phthalocyanine

5. TYPE OF REPORT & PERIOD COVERED
Interim

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(*s*)
H. Nakai and M. Tsutsui*

8. CONTRACT OR GRANT NUMBER(*s*)
N00014-75-C-0417

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
Texas A&M University
College Station, Texas 77843

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 053-559

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

12. REPORT DATE
October 1978

13. NUMBER OF PAGES
13

14. MONITORING AGENCY NAME & ADDRESS(*If different from Controlling Office*)

15. SECURITY CLASS. (*of this report*)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for Public Release; Distribution Unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

ONR Technical Report

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Charge Transfer Complexes of Phthalocyanines
hexadecafluorophthalocyanine

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

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

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

# Charge Transfer Complexes of Phthalocyanine

H. Nakai and M. Tsutsui*
Texas A&M University
Chemistry Department
College Station, Texas 77843

## 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 skewered complex.[1-4] Metallo-organic polymers have the potential to be one dimensional conductors with metal-like conductivity.[5] The best one dimensional conductors known so far are those with equivalent molecules in stacks.[6] These compounds are formed from $d^8$ 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 skewered 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[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 phthalocycanine ligands in a manner similar to tin (IV) bis(phthalocyanine), 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.[8,9] Recently, the structures of bis(phthalocyanine) uranium (IV)[10] and bis(phthalocyanine) tin (IV)[11] 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 moisture and like the mercury complex[12] may possess potential use in the formation of polymers.

Metalloporphyrins are reported to form charge transfer complexes with strong electron acceptors such as $Ni(S_2C_2(CF_3)_2)_2(Ni(tfd)_2)$[13], trinitroarenes,[14] tetracyanoethylene,[15] and tetracyanoquinodimethane.[16] Copper phthalocyanine polymer has the highest mobility, a parameter of electronic conductivity, of any organometallic compound. One difficulty of phthalocyanine chemistry is its insolubility towards organic solvents. This presents 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.[17,18,19] 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 organometallophthalocyanines with strong electron donor or acceptor characters. Some of the former compounds are metallotetraazaporphines, metallocta-zaphthalocyanines, etc., and the latter metallophthalocyanines, metallohexadecafluorophthalocyanines, 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.[20] 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

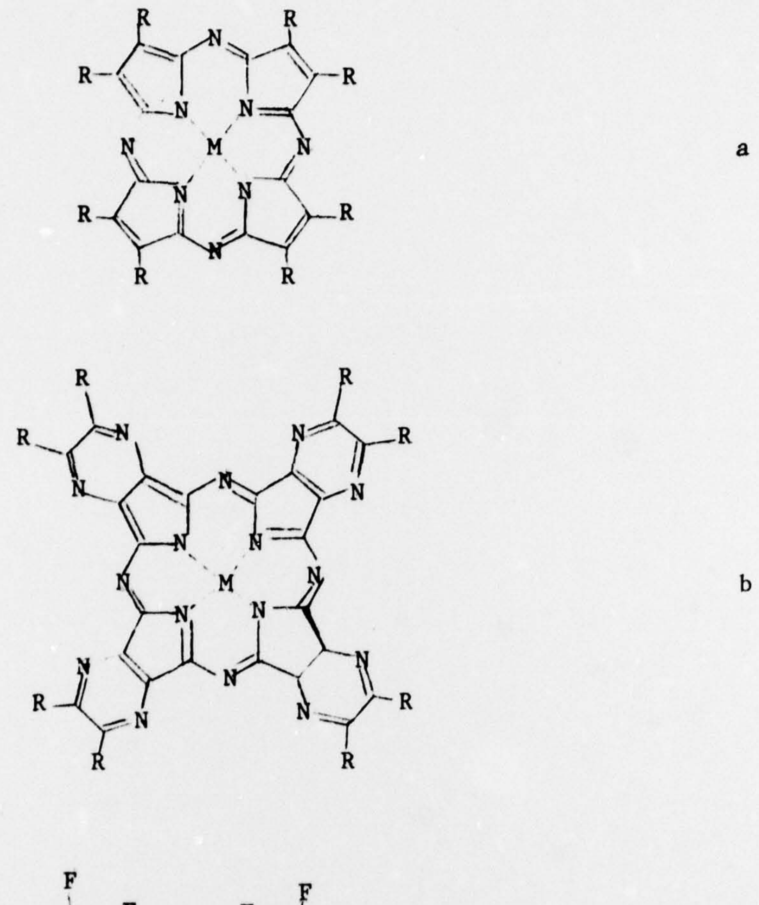

Figure 1

Figure 1

a. Metallotetraazaporphines
b. Metallooctaazaphthalocyanines
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 octamethyltetrapyrazinoporphyrazine were therefore studied.

When 2,d-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. $H_2SO_4$, 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,[20] 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,[17] 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 tetraflouorophthalonitrile 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 dessiccator.

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.

### Magensium 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. $H_2SO_4$.

## 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 identiried 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 rutheniumcarbonylperfluorophthalocyanine. TLC showed that the product was not chromiumperfluorophthalocyanine.

### 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.

## ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

## References

1. D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, J. Am. Chem. Soc., 94, 1385 (1972).
2. D. Cullen, E. Meyer, S. Srivastava, and M. Tsutsui, J. Am. Chem. Soc., 94, 620 (1977).
3. M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Meyer, Jr., J. Am. Chem. Soc., 97, 3952 (1975).
4. S. Kato, M. Tsutsui, D. L. Cullen, and E. F. Meyer, Jr., J. Am. Chem. Soc., 99, 620 (1977).
5. J. S. Miller and A. J. Epstein, Prog. Inorg. Chem., 20, 1 (1976).
6. J. S. Miller, Inorg. Chem., 15, 2357 (1976).
7. F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds," ACS Monograph 157, Reinhold, New York, 1973.
8. S. Misumi and K. Kasuga, Nippon Kagaku Zasshi, 92, 335 (1971).
9. F. Lux, "Proceedings of the 10th Rare Earth Research Conference," Vol. II, Apr. 30-May 3, 1977, p. 881.
10. A. Gieren and W. Hoppe, J. Chem. Soc., Chem. Commun., 413 (1971)
11. W. E. Bennett, D. E. Broberg, and N. C. Baenziger, Inorg. Chem., 12, 930 (1973).
12. M. F. Hudson and K. M. Smith, J. Chem. Soc., Chem. Commun., 515 (1973).
13. G. M. Shkolnik and W. E. Geiger, Jr., Inorg. Chem., 14, 313 (1975).
14. H. A. O. Hill, A. J. Macfarlane, and R. J. P. Williams, J. Chem. Soc. (A), 1704 (1969).
15. B. B. Wayland and D. Mohajer, Inorg. Nucl. Chem. Letters, 633 (1973).
16. A. N. Sidorov, Biofizika, 19, 45 (1974).
17. R. Taube, Z. Chem., 6, 8 (1966).
18. Y. Bansho, Kogyo Kagaku Zasshi, 74, 150 (1971).
19. J. Manassen, Cat. Rev.-Sci. Eng., 9, 223 (1974).
20. M. Tsutsui and S. Omiya, J. Am. Chem. Soc., in preparation.

# APPENDIX

472:GAN:716:tam
78u472-608

## TECHNICAL REPORT DISTRIBUTION LIST, GEN

| | No. Copies |
|---|---|
| Office of Naval Research<br>800 North Quincy Street<br>Arlington, Virginia 22217<br>Attn: Code 472 | 2 |
| ONR Branch Office<br>536 S. Clark Street<br>Chicago, Illinois 60605<br>Attn: Dr. George Sandoz | 1 |
| ONR Branch Office<br>715 Broadway<br>New York, New York 10003<br>Attn: Scientific Dept. | 1 |
| ONR Branch Office<br>1030 East Green Street<br>Pasadena, California 91106<br>Attn: Dr. R. J. Marcus | 1 |
| ONR Area Office<br>One Hallidie Plaza, Suite 601<br>San Francisco, California 94102<br>Attn: Dr. P. A. Miller | 1 |
| ONR Branch Office<br>Building 114, Section D<br>666 Summer Street<br>Boston, Massachusetts 02210<br>Attn: Dr. L. H. Peebles | 1 |
| Director, Naval Research Laboratory<br>Washington, D.C. 20390<br>Attn: Code 6100 | 1 |
| The Assistant Secretary<br>of the Navy (R,E&S)<br>Department of the Navy<br>Room 4E736, Pentagon<br>Washington, D.C. 20350 | 1 |
| Commander, Naval Air Systems Command<br>Department of the Navy<br>Washington, D.C. 20360<br>Attn: Code 310C (H. Rosenwasser) | 1 |
| Defense Documentation Center<br>Building 5, Cameron Station<br>Alexandria, Virginia 22314 | 12 |
| U.S. Army Research Office<br>P.O. Box 1211<br>Research Triangle Park, N.C. 27709<br>Attn: CRD-AA-IP | 1 |
| Naval Ocean Systems Center<br>San Diego, California 92152<br>Attn: Mr. Joe McCartney | 1 |
| Naval Weapons Center<br>China Lake, California 93555<br>Attn: Dr. A. B. Amster<br>Chemistry Division | 1 |
| Naval Civil Engineering Laboratory<br>Port Hueneme, California 93401<br>Attn: Dr. R. W. Drisko | 1 |
| Professor K. E. Woehler<br>Department of Physics & Chemistry<br>Naval Postgraduate School<br>Monterey, California 93940 | 1 |
| Dr. A. L. Slafkosky<br>Scientific Advisor<br>Commandant of the Marine Corps<br>(Code RD-1)<br>Washington, D.C. 20380 | 1 |
| Office of Naval Research<br>800 N. Quincy Street<br>Arlington, Virginia 22217<br>Attn: Dr. Richard S. Miller | 1 |
| Naval Ship Research and Development<br>Center<br>Annapolis, Maryland 21401<br>Attn: Dr. G. Bosmajian<br>Applied Chemistry Division | 1 |
| Naval Ocean Systems Center<br>San Diego, California 91232<br>Attn: Dr. S. Yamamoto, Marine<br>Sciences Division | 1 |

Encl 1

## TECHNICAL REPORT DISTRIBUTION LIST, 053

No. Copies

Dr. R. N. Grimes
University of Virginia
Department of Chemistry
Charlottsville, Virginia 22901 1

~~Dr. M. Tsutsui~~
~~Texas A&M University~~
~~Department of Chemistry~~
~~College Station, Texas 77843~~ 1

Dr. M. F. Hawthorne
University of California
Department of Chemistry
Los Angeles, California 90024 1

Dr. D. B. Brown
University of Vermont
Department of Chemistry
Burlington, Vermont 05401 1

Dr. W. B. Fox
Naval Research Laboratory
Chemistry Division
Code 6130
Washington, D.C. 20375 1

Dr. J. Adcock
University of Tennessee
Department of Chemistry
Knoxville, Tennessee 37916 1

Dr. A. Cowley
University of Texas
Department of Chemistry
Austin, Texas 78712 1

Dr. W. Hatfield
University of North Carolina
Department of Chemistry
Chapel Hill, North Carolina 27514 1

Dr. D. Seyferth
Massachusetts Institute of
Technology
Department of Chemistry
Cambridge, Massachusetts 02139 1

No. Copies

Dr. M. H. Chisholm
Department of Chemistry
Indiana University
Bloomington, Indiana 47401 1

Dr. B. Foxman
Brandeis University
Department of Chemistry
Waltham, Massachusetts 02154 1

Dr. T. Marks
Northwestern University
Department of Chemistry
Evanston, Illinois 60201 1

Dr. G. Geoffrey
Pennsylvania State University
Department of Chemistry
University Park, Pennsylvania 16802 1

Dr. J. Zuckerman
University of Oklahoma
Department of Chemistry
Norman, Oklahoma 73019 1

Professor O. T. Beachley
Department of Chemistry
State University of New York
Buffalo, New York 14214 1

Professor P. S. Skell
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802 1

Professor K. M. Nicholas
Department of Chemistry
Boston College
Chestnut Hill, Massachusetts 02167 1