

AD-A064 163

NORTH CAROLINA UNIV AT CHAPEL HILL DEPT OF CHEMISTRY F/G 7/3
THE STRUCTURE AND MAGNETIC AND ELECTRICAL CONDUCTIVITY PROPERTIES--ETC(U)
JAN 79 S R WILSON, P J CORVAN, R P SEIDERS N00014-76-C-0816

UNCLASSIFIED

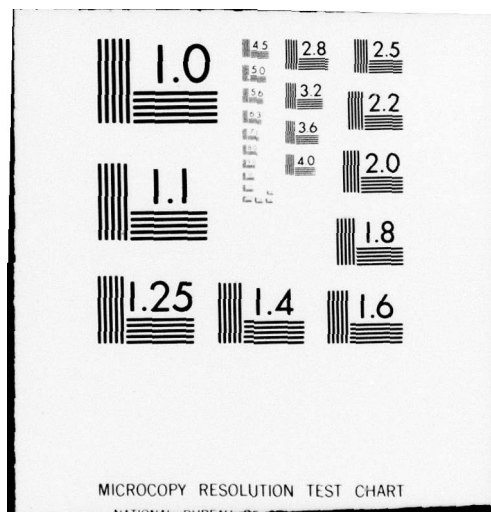
TR-5

NL

1 OF 1
AD
A064163



END
DATE
FILMED
3-79
DDC



LEVEL

OFFICE OF NAVAL RESEARCH

Contract ¹⁵ N00014-76-C-0816

Project .NR 053-617

⁹ TECHNICAL REPORT, NO. 5

⁶ The Structure and Magnetic and Electrical Conductivity Properties of the Charge Transfer Compound 1,1'-Dimethylferrocenium Bis(Tetracyanoquinodimethane),
 $[(CH_3C_5H_4)_2Fe][TCNQ]_2$.

by

¹⁰ Scott R. Wilson, Peter J. Corvan, Reginald P. Seiders, Derek J. Hodgson,
Maurice Brookhart, William E. Hatfield, Joel S. Miller, Arthur H. Reis, Jr.,
P.K. Rogan, Elizabeth Gebert and Arthur J. Epstein

Prepared for Publication

in

The Proceedings of a NATO Advanced Research Institute on Molecular Metals
Les Arcs, France, 1978

University of North Carolina

Department of Chemistry

Chapel Hill, North Carolina

¹¹ 15 January 15, 1979

¹² 12p.

¹⁴ TIR-5

DDC
RECEIVED
FEB 5 1979
C

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

Approved for Public Release: Distribution Unlimited

400 342

79 01 25 028

LB

DDC FILE COPY.
A064163

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Structure and Magnetic and Electrical Conductivity Properties of the Charge Transfer Compound 1,1'-Dimethylferrocenium Bis(Tetracyanoquinodimethane), $[(CH_3)_2C_5H_4]_2Fe[TCNQ]_2$		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) Scott R. Wilson, Peter J. Corvan, Reginald P. Seiders, Derek J. Hodgson, Maurice Brookhart, William E. Hatfield, Joel S. Miller, Arthur H. Reis, Jr., P.K. Rogan, Elizabeth Gebert and Arthur I. Epstein		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of North Carolina Chapel Hill, NC 27514		8. CONTRACT OR GRANT NUMBER(s) N0014-76-C-0816
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-617
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 16, 1979
		13. NUMBER OF PAGES 8
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
15. 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		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Conductivity, magnetic susceptibility, crystal structure, organometallic compounds, ferrocene, tetracyanoquinodimethane,		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The charge transfer compound 1,1'-dimethylferrocenium bis(tetracyanoquinodimethane) has been prepared and characterized by a single crystal x-ray structure determination, magnetic susceptibility studies, and conductivity measurements. The structure consists of chains of stacked TCNQ molecules and stacked ferrocenium ions, but there are no intermolecular interactions in the latter chains.		

ACCESS TO:	
NTIS	Ref Section ☒
DOC	B. H. Section ☐
UNANNOUNCED	☐
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	SPECIAL
A	

THE STRUCTURE AND MAGNETIC AND ELECTRICAL CONDUCTIVITY PROPERTIES
OF THE CHARGE TRANSFER COMPOUND 1,1'-DIMETHYLFERROCENIUM BIS-
(TETRACYANOQUINODIMETHANE), $[(CH_3C_5H_4)_2Fe][TCNQ]_2$.

Scott R. Wilson,^a Peter J. Corvan,^a Reginald P. Seiders,^a
Derek J. Hodgson,^a Maurice Brookhart,^a William E.
Hatfield,^a Joel S. Miller,^b Arthur H. Reis, Jr.,^c
P. K. Rogan,^c Elizabeth Gebert^c and Arthur J. Epstein^d

Kenan Laboratory 045A, University of North Carolina,
Chapel Hill, NC 27514^a

Rockwell Science Center, Thousand Oaks, CA 91360^b

Argonne National Laboratory, Argonne, IL 60439^c

Xerox Webster Research Center, Rochester, NY 14644^d

Metallocenes react with tetracyanoquinodimethane (TCNQ) to yield charge transfer compounds predominantly of the stoichiometry $[metallocene][TCNQ]$ or $[metallocene][TCNQ]_2$.^{1,2} The 1:2 compounds have relatively high electrical conductivities which range from 4 $ohm^{-1}cm^{-1}$ for $[(C_5H_5)_2Fe][TCNQ]_2$ to 0.03 $ohm^{-1}cm^{-1}$ for $[(CH_3C_5H_4)_2Fe][TCNQ]_2$,¹ but, up to now, difficulties in obtaining high quality single crystals have prevented structural determinations.

The recent report³ of the use of Sephadex gels for the growth of single crystals led us to use this technique in the case of $[(CH_3C_5H_4)_2Fe][TCNQ]_2$.

Experimental Section:

The title charge-transfer complex was prepared by reaction of 1,1'-dimethylferrocene and TCNQ (molar ratio 1:2, respectively) in hot acetonitrile solution. Dark needles were isolated by filtration of the cooled solution. A portion of this material was dissolved in a minimum volume of hot acetonitrile and the resulting dark green solution was poured into a warm test tube (1.5 x 12 cm). Immediately, Sephadex LH-20 (Pharmacia Fine Chemicals) was added until all the acetonitrile had been absorbed. The test tube was allowed to cool slowly, and within 30 minutes small rectangular prisms of the complex began growing inside the gel. After one day at room temperature, the gel was then broken up with distilled water

79 01 25 028

and individual crystals were removed for study.

For the preparation of dimethylferrocenium hexafluorophosphate, dimethylferrocene (4.0 mmole) was oxidized by stirring in dilute nitric acid for 2 hours at which time dissolution was nearly complete. The addition of ammonium hexafluorophosphate to the filtered solution produced a blue-grey precipitate of the PF_6^- salt. This material was then rapidly recrystallized from anhydrous methanol to give 0.22 g (15% yield) of the PF_6 salt as a green-grey powder, whose formulation was confirmed by elemental analysis.

Magnetic properties were measured using a PAR vibrating sample magnetometer. Temperatures were measured with a calibrated gallium/arsenide diode by observing the voltage on a Dana Model 4700 4.5 place digital voltmeter. Details of the experimental techniques have been given elsewhere.⁴

Crystallographic Section:

Two entirely separate sets of data were collected, one at Argonne National Laboratory and the other at the University of North Carolina; the following discussion pertains to the latter set, since these data were obtained from a crystal synthesized by the method described above. The two data sets are, however, of comparable quality, and the derived structural parameters are equal with standard deviations.

On the basis of precession and Weissenberg photography, the intensely dark blue prismatic crystals were assigned to the triclinic system, the space group being either $\text{P}\bar{1}$ or $\text{P}1$; the former choice was confirmed by the successful refinement of the structure. The cell constants, obtained by least-squares methods from the diffractometer settings of twelve reflections with $2\theta(\text{Mo}) > 25^\circ$, are $a = 7.660(2)$, $b = 7.530(2)$, $c = 14.083(4)$ Å, $\alpha = 83.83(2)^\circ$, $\beta = 110.42(2)^\circ$, $\gamma = 94.48(2)^\circ$. The observations were made at 22°C with the wavelength assumed as $\lambda(\text{MoK}\alpha_1) = 0.70926$ Å. A density of $1.35(1)$ g cm^{-3} observed by flotation in chloroform/dichloromethane solutions is in acceptable agreement with the value of 1.370 g cm^{-3} calculated for one formula unit per cell. Hence, in space group $\text{P}\bar{1}$ the iron atom is constrained to lie on a crystallographic inversion center.

Diffraction data were collected from a prismatic crystal bounded by the (001), (00 $\bar{1}$), (100), ($\bar{1}00$), (010), and (01 $\bar{1}$) faces. The approximate crystal dimensions were 0.51 x 0.16 x 0.11 mm in the [100], [001], and [010] directions, respectively. The crystal was mounted approximately parallel to the crystallographic a axis, and intensity data were collected on a Picker four circle automatic diffractometer equipped with a molybdenum tube and a graphite monochromator. Data were collected by the $\theta/2\theta$ scan technique at a

scan rate of $1.0^\circ \text{min}^{-1}$. To allow for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, peaks were scanned from 1.0° in 2θ below the calculated $K\alpha_1$ peak position to 1.0° in 2θ above the calculated $K\alpha_2$ peak position. Stationary-counter, stationary-crystal backgrounds were counted for 20s at each end of the scans. A unique data set having $2\theta(\text{MoK}\alpha) \leq 55^\circ$ was gathered, a total of 3747 reflections being collected. The intensities of three standard reflections, examined after every 100 reflections, remained essentially constant throughout the run.

The data were processed by the method of Ibers and coworkers.⁵ After correction for background, the intensities were assigned standard deviations as

$$\sigma(I) = [C + 0.25(ts/tb)^2(B_H + B_L) + (pI)^2]^{1/2}$$

where the symbols have their usual meanings⁵ and the value of p was assigned as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects⁶ and for absorption.⁷ The absorption coefficient μ for these atoms with $\text{MoK}\alpha$ radiation is 5.28 cm^{-1} , and for the sample chosen the transmission coefficients ranged from 0.92 to 0.96. Of the 3747 intensities recorded, only 1599 were independent data with $I > 3\sigma(I)$; only these data were used in the structure analysis.

The structure was solved by direct methods using the highest 256 normalized structure amplitudes (E 's) in the program MULTAN.⁸ Because of some pseudo symmetry, the data with $h = 2n$ had to be scaled separately from those with $h = (2n + 1)$. The resulting E-map revealed the locations of the TCNQ carbon atoms and the iron atom (constrained to lie on an inversion center). Isotropic refinement of these positions led to values of the conventional agreement factors $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$ of 0.281 and 0.364, respectively. All least-squares refinements were on F , the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ with the weight w being assigned as $4F_o^2/\sigma^2(F_o^2)$. The scattering factors were taken from the usual sources.⁹

The carbon atoms of the methylcyclopentadienyl moiety were located in a difference Fourier map. Eventual anisotropic refinement of these atoms led to $R_1 = 0.072$, $R_2 = 0.077$. Addition of the four hydrogen atoms in the TCNQ moiety, refined isotropically, gave $R_1 = 0.064$, $R_2 = 0.065$. At this stage of refinement the C-C ring bond lengths in the methylcyclopentadienyl moiety were rather short, ranging from 1.33 to 1.39 Å, and the U_{ij} 's were very large; these observations could be attributable to some disorder, which is extremely common for systems of this type,¹⁰ but attempts to refine a disordered model were unsuccessful. Addition of the remaining

hydrogen atoms led to $R_1 = 0.059$; a difference Fourier at this stage was featureless with no peak higher than 0.5 eA^{-3} .

Description of the Structure:

The structure consists of $\text{Fe}(\text{CH}_3\text{C}_5\text{H}_4)_2$ and TCNQ units. The iron atom lies on a crystallographic inversion center. The TCNQ moieties also lie on inversion centers, there being two crystallographically independent "half-TCNQ" moieties. The packing of these fragments in the crystal is shown in Figures 1 and 2. As is seen in Figure 2, one TCNQ unit (A) approaches neighboring iron atoms (through its terminal CN groups) much more closely than does the

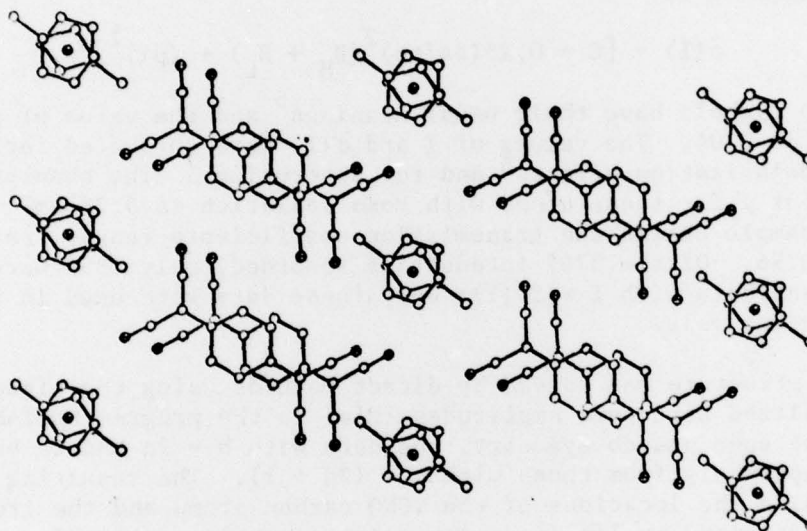


Figure 1. A view of structure of 1,1'-dimethylferrocenium (TCNQ)₂ along the *a* axis which shows the slipped nature of the TCNQ stacks.

other (B). As is seen in the figures, the structure can be viewed as consisting of chains of $\text{CH}_3\text{C}_5\text{H}_4$ (MeCp) rings separated by parallel chains of TCNQ units; the direction of the chains is the crystallographic *a*-axis. The MeCp and TCNQ rings are not normal to the chain direction, however; in the MeCp chain the angle between the normal to the planes and the *a*-axis is 9.1° , while in the TCNQ chain the average value is 14.2° .

In the MeCp chains, there are two distinct separations; the rings involved with any given Fe atom are separated by $3.41 \text{ \AA}$

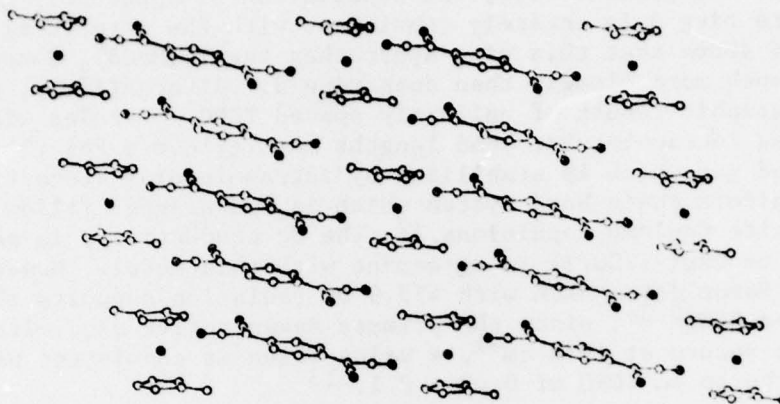


Figure 2. A view of the structure of 1,1'-dimethylferrocenium (TCNQ)₂ along the *b* axis which shows the parallel stacks of ferrocenium ions and TCNQ units.

while neighboring rings are separated by 3.63 Å. The units in the TCNQ chains are equally spaced, the center of each ring lying on an inversion center; the separation between each ring center is simply $a/2$ as measured along *a*. Since the rings are not normal to the chain direction, however, the interplanar separation is only 3.23 Å.

The two TCNQ units are crystallographically distinct and are much more precisely determined than the MeCp rings because of the high thermal motion (or disorder) of the latter. The rings each display the expected quinoidal geometry, with two "double" bonds and four "single" bonds. In the A ring these are of lengths 1.343(7) and 1.425(6) and 1.433(6) Å, respectively, while in the B ring the values are 1.334(7), 1.436(6), and 1.438(6) Å, respectively. The four terminal C-N bond lengths are all very similar, with values of 1.139(6), 1.139(6), 1.140(6), and 1.145(6) Å. There appears to be a significant difference, however, between the extracyclic, nominally double, C-C bonds in the two rings; in ring A this has the length 1.395(6) Å, while in ring B it is 1.378(6) Å. This small but significant difference, which is independently confirmed in the Argonne analysis, has been observed by other workers in related systems¹¹ and can be attributed to an increase in radical character on ring A relative to that on B. In neutral TCNQ this distance is 1.374 Å, in TCNQ⁻ it is 1.418 Å and in the system reported as TCNQ_{1/2}⁻ it is 1.388 Å; hence, it is apparent that this C=C distance is

extremely sensitive to electron donation from donors in the crystal.¹¹ In the present case, the observation of apparently greater donation to ring A is entirely consistent with the structural feature noted above that this ring approaches the $\text{Fe}(\text{MeCp})_2$ donor moieties much more closely than does ring B. Alternatively, this crystallographic result of uniformly spaced TCNQ molecules with alternating intramolecular bond lengths may reflect a Peierls distortion and gap which is stabilized by intramolecular distortion in this uniform chain band system which is one-quarter filled with large on-site Coulomb repulsions.¹² The dc conductivity is proportional to $\exp(-1200/T)$ in agreement with this model. However, resonance Raman data taken with 457.9 nm radiation supports the formulation $\text{TCNQ}^{0.5-}$, since the primary Raman active exocyclic C-C absorption occurs at 1428 cm^{-1} , a value which is consistent with a negative charge on TCNQ of 0.42 ± 0.1 .¹³

Magnetic Properties:

The temperature variation of the magnetic susceptibility of a powdered sample of $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Fe}][\text{TCNQ}]_2$ was determined in the temperature range 4.2 to 76°K. The data are presented in Figure 3 as a plot of the reciprocal of the molar susceptibility versus temperature. The data may be fit very precisely by the Curie-Weiss Law

$$\chi = \frac{C}{T-\theta}$$

where $C = N g^2 \beta^2 S(S+1)/3k$ with $g = 2.837$ and $\theta = -0.732^\circ$. The best fit of the Curie-Weiss Law to the data is shown as the solid line in Figure 3. The average g value determined from the magnetic susceptibility data agrees nicely with an average g value of 2.79 which may be calculated from the EPR data for 1,1'-dimethylferrocenium hexafluorophosphate using the expression

$$g_{\text{ave}}^2 = 1/3(g_{\parallel}^2 + 2g_{\perp}^2)$$

and the observed $g_{\parallel} = 4.002$ and $g_{\perp} = 1.92$.¹⁴ For the purpose of comparison, magnetic susceptibility data for 1,1'-dimethylferrocenium hexafluorophosphate are plotted as open squares in Figure 3. The close agreement of the data for the two compounds leads to the conclusion that the susceptibility in this temperature region is dominated by the 1,1'-dimethylferrocenium cation, and more remarkably, to the conclusion that these cations, although packed closely in the crystal structure, do not exhibit appreciable intermolecular spin-spin interactions.

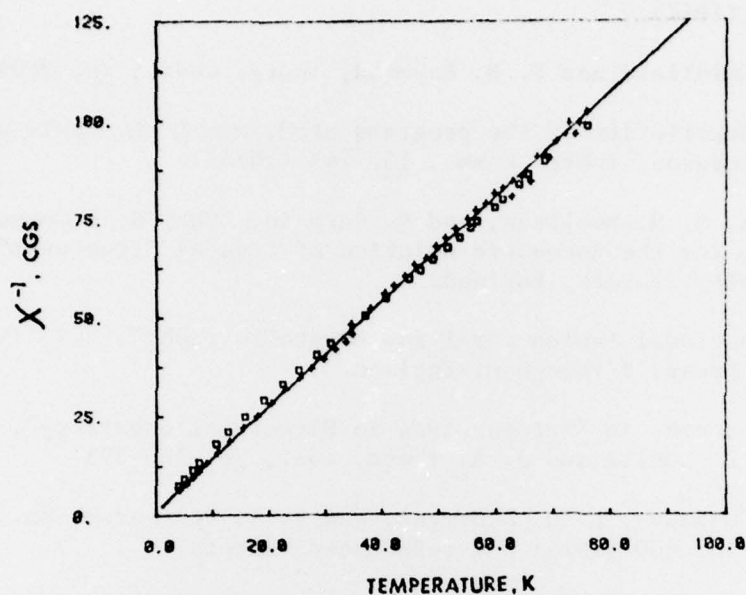


Figure 3. The inverse susceptibility of 1,1'-dimethylferrocenium (TCNQ)₂ (+) and 1,1'-dimethylferrocenium (PF₆)₂ (□) as a function of temperature. The solid line is the best fit to the Curie-Weiss law for the TCNQ charge transfer compound.

Acknowledgement

This work was supported in part by the Office of Naval Research, the National Science Foundation, and the Department of Energy.

References

1. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).
2. J. S. Miller, A. H. Reiss, Jr., and G. A. Candela, *Lecture Notes in Physics*, in press.
3. G. R. Desiraju, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **99**, 6148 (1977).
4. D. B. Losee and W. E. Hatfield, *Phys. Rev. B*, **10**, 212 (1974).
5. P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*,

- 6, 197 (1967).
6. S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 10, 2604 (1971).
 7. For a description of the programs used, see D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, 13, 143 (1974).
 8. P. Main, M. M. Woolfson, and G. Germain, "MULTAN: A Computer Program for the Automatic Solution of Crystal Structures", University of York, England.
 9. "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England.
 10. F. Herbststein, in "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, eds., pp. 166-395.
 11. R. P. Shibaeva, L. O. Atovmyan, and V. I. Ponomarev, *Zh. Str. Khim.*, 16, 860 (1975) and references therein.
 12. E. M. Connell, A. J. Epstein, and M. J. Rice, *Proc. Int. Conf. on Quasi-One-Dimensional Conductors*, Dubrovnik, Yugoslavia, Sept. 4-8, 1978. (Springer-Verlag, to be published).
 13. T. W. Cape and R. P. Van Dyne, private communication.
 14. D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 14, 955 (1975).

TECHNICAL REPORT DISTRIBUTION LIST, GEN

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

TECHNICAL REPORT DISTRIBUTION LIST, 053

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. N. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia 22901	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1	Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1	Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. D. B. Brown University of Vermont Department of Chemistry Burlington, Vermont 05401	1	Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D.C. 20375	1	Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee 39716		Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	;