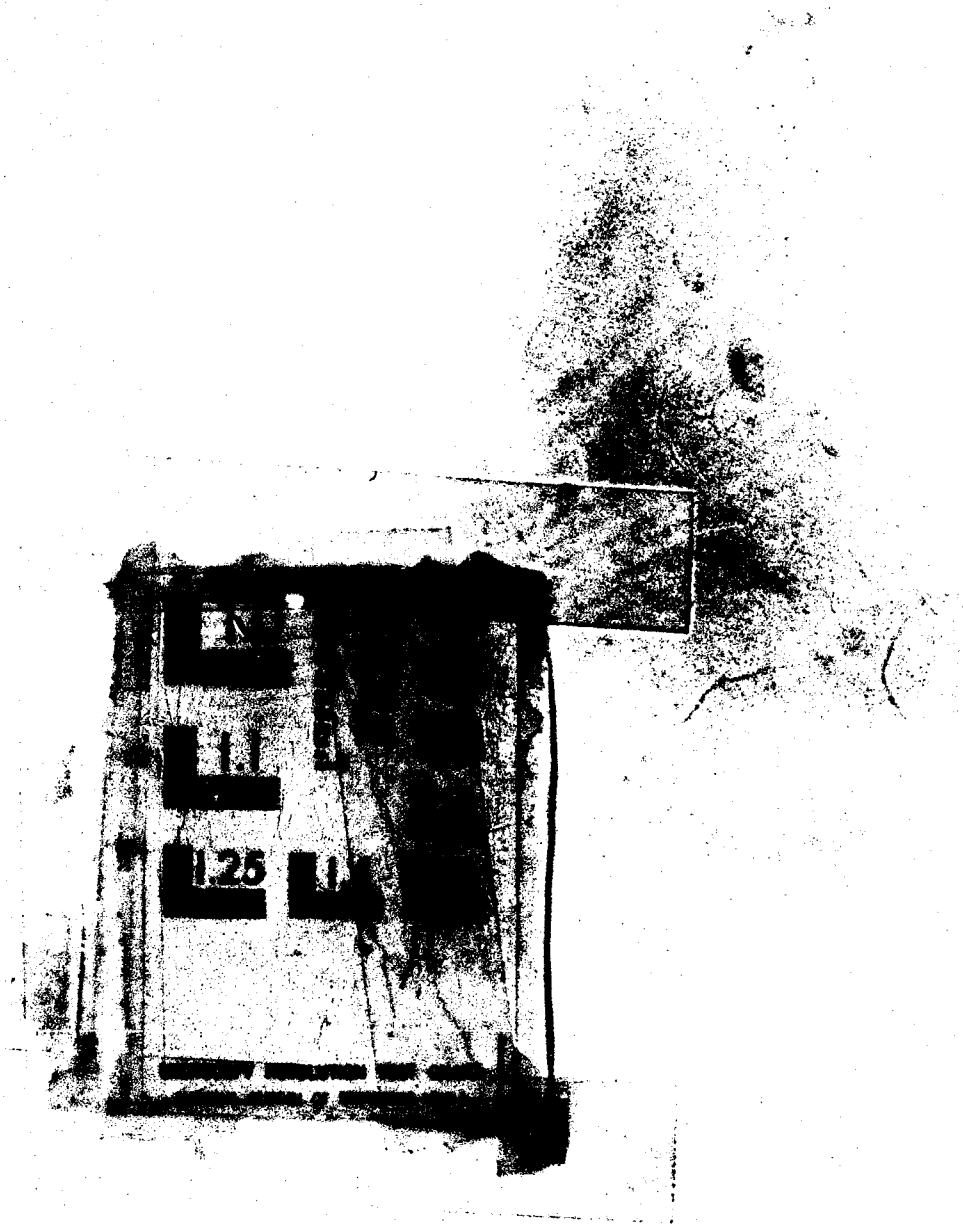
AD-A157 164 THE INTERACTION OF COMPLEXES MN(PPHME2)BR2 AND MN(PET3)BR2 WITH SULFUR DIOXIDE(U) AUBURN UNIV AL DEPT OF CHEMISTRY W E HILL ET AL. 18 JUL 85 1/1

UNCLASSIFIED N00014-83-K-0637 F/G 7/4 NL

END


1.25

AD-A157 164

(2)

The Interaction of Complexes $Mn(PPhMe_2)Br_2$ and $Mn(PEt_3)Br_2$ with Sulfur Dioxide

W.E. Hill*, S.D. Worley*, and D.K. Paul
Department of Chemistry, Auburn University,
Auburn, AL 36849

and

V.F. Newberry, Department of Natural Science,
Eastern Montana College, Billings, Montana 59101

Abstract

The interactions of the complexes $Mn(PPhMe_2)Br_2$ and $Mn(PEt_3)Br_2$ as films with SO_2 and $S^{18}O_2$ have been investigated using infrared spectroscopy as an analytical probe. It is clear from these preliminary studies that two types of complexes with SO_2 have been formed. When the $MnLBr_2$ films were exposed to low pressures of SO_2 for relatively short times, an $MnLBr_2/SO_2$ complex formed reversibly in that the SO_2 could be removed by prolonged evacuation. On the other hand, lengthy exposure of the $MnLBr_2$ films to higher pressures of SO_2 caused the irreversible formation of a complex having stoichiometry $MnLBr_2 \cdot 1/2SO_2$. It is probable that the SO_2 bonds in some type of bridging fashion in both of the types of $MnLBr_2/SO_2$ complexes.

DTIC FILE COPY

DTIC ELECTE AUG 2 1985 S D

This document has been approved for public release and sale; its distribution is unlimited.

85 7 22 075

There has been considerable recent interest in complexes of the form $MnLX_2$ (L=tertiary phosphine, X=anion) and their interaction with dioxygen.[1,2] Infrared work in these laboratories concerning films of the complexes has shown that the complexes do exist and that some do interact reversibly with dioxygen, the extent of which is markedly dependent upon the nature of the tertiary phosphine ligand.[3,4] All of the complexes studied here, however, exhibit competing irreversible decay channels at room temperature to the corresponding phosphine oxide complexes.[3,4] The purpose of this note is to report infrared data concerning the interaction of the complex films with sulfur dioxide.

The complex films studied here were prepared by sublimation of $MnBr_2$ onto a KBr infrared window followed by heating to ca. 473 K in a specially designed infrared cell[3,4] at 10^{-6} Torr to remove all water. Then the dry $MnBr_2$ films were exposed to either $PPhMe_2$ or PEt_3 in vacuo to form the $MnLX_2$ complex films. Extensive evacuation at 10^{-6} Torr was employed to remove all traces of excess phosphine. The films thus prepared were exposed to SO_2/evacuation cycles with infrared spectra (Perkin-Elmer Models 580 or 983 with data station) being monitored at appropriate intervals. Since $SO_2(g)$ exhibits infrared bands near 520, 1150, and 1360 cm^{-1} which might have interfered with resolution of the complex bands, the cell was always briefly evacuated following SO_2 exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the $Mn(PPhMe_2)Br_2$ complex film interacting with SO_2. A comparison of Fig. 1b and 1a reveals that new infrared bands at $SO_2(S^{18}O_2)$: 412(410), 445(440), 525(515), 785(780), 995(950), 1002(968), and 1075(1028) cm^{-1} appear which can be attributed to a new complex(es) formed from the reaction of SO_2 with

DTIC FILE COPY

[illegible] The [illegible] band at 1155 cm^{-1} in 1b which does not shift [illegible] can be assigned to a ligand vibrational mode ($\nu_{PC\ aryl}$) which is accentuated due to the presence of SO_2; this band was also observed to be enhanced by the presence of dioxygen.[4] All of the bands mentioned above declined markedly upon evacuation at 10^{-6} Torr for 18 hr (Fig. 1c). We have been able to observe cycling of the intensities of these bands upon reexposure/evacuation for up to three cycles; ca. 12 hr evacuation is required to essentially remove the SO_2. However, upon lengthy exposure (72 hr) at high pressure (120 Torr) spectrum 1d resulted which could not be reversed by lengthy evacuation. The bands at 995, 1002, and 1075 cm^{-1} for [illegible] when $S^{18}O_2$ is used and obviously correspond to S-O stretching vibrational modes; the fact that three such bands were present indicates that more than one type of complex is probably being formed. [illegible] the bands at 612 and 445 cm^{-1} shifted little upon isotopic substitution; these bands could correspond to Mn-S modes. The bands at [illegible] cm^{-1} in 1b and 625 cm^{-1} in 1d did shift appreciably when $S^{18}O_2$ was [illegible] and probably correspond to Mn-O modes.

Figure 2 shows a similar series of experiments for $Mn(PEt_3)Br_2$ interacting with SO_2. Band positions for $S^{18}O_2$ complex spectra are shown in parentheses. Again reversibility was observed as long as exposure time and pressure were minimized. It is clear that at least two types of $MnLBr_2/SO_2$ complexes were formed in these experiments - one in which the SO_2 bonds reversibly and one in which the SO_2 is coordinated in an irreversible fashion. Comparison of the intensities of the 865, 910, and 970 cm^{-1} bands in spectra 2d and 2e reveals that the reversible complex can decompose to the irreversible one even during evacuation following high SO_2 exposures.

Bulk samples of the two final irreversible SO_2 complexes were prepared [illegible] in a manner completely analogous to the sample treatment conditions for the complex films. The bulk analyses of the two final irreversible SO_2 complexes revealed that the stoichiometry for each was $MnLSr_2 \cdot 1/2SO_2$.[5] This data along with the observation of intense infrared bands in the 800-1075 cm^{-1} regions of the spectra imply that the two forms of each complex contain SO_2 bonded in a bridging mode,[6] with more than one atom of SO_2 involved in the bridge. Final structure determination must await X-ray crystallographic data.

It should be noted that McAuliffe and coworkers have reported recently the reaction of SO_2 with several $MnLX_2$ complexes in toluene solution and in toluene slurries.[7] They report a stoichiometry of $MnLX_2 \cdot 2/3SO_2$ for their solution studies, and they were not able to observe reversibility. Furthermore, they report prominent infrared bands in the 1112-1140 cm^{-1} region which are not observed for the $MnFEt_3Sr_2/SO_2$ complex film. However, their experimental conditions (liquid phase, 760 Torr SO_2 exposure for 48 hr) were markedly different than those used in this work; thus it is possible that a reversible complex was formed also in their work, but converted to an irreversible product before analysis.

Acknowledgement

The authors are grateful to the Office of Naval Research, the Research Corporation, and the Auburn University Energy Grant-In-Aid program for partial support of this work. They also thank C.A. McAuliffe for a preprint of reference 7.

REFERENCES

(1) McAuliffe, C.A. J. Organomet. Chem. 1982, 228, 255 and numerous references quoted therein.

(2) Bryan, R.M.; Bull, R.H.; Green, M.L.H.; Grebenik, P.D.; Martin-Polo, J.J.; Mingos, D.M.P. J. Organomet. Chem. 1980, 201, 437.

(3) Burkett, H.D.; Newberry, V.F.; Hill, W.E.; Worley, S.D. J. Amer. Chem. Soc. 1983, 105, 4097.

(4) Newberry, V.F.; Burkett, H.D.; Worley, S.D.; Hill, W.E. Inorg. Chem. 1984, 23, 3911.

(5) Anal. Calcd (Atlantic Microlabs, Inc.) for $Mn(PPhMe_2)Br_2 \cdot 1/2SO_2$: C 25.0, H 2.9, Br 41.5, S 4.2. Found: C 24.8, H 3.0, Br 41.4, S 4.1; Anal. Calcd (Atlantic Microlabs, Inc.) for $Mn(PEt_3)Br_2 \cdot 1/2SO_2$: C 19.7, H 4.1, Br 43.8, S 4.4. Found C 19.7, H 4.2, Br 43.7, S 4.4.

(6) See for examples: Vitzthum, G.; Lindner, E. Angew. Chem. Int. Edit. 1971, 10, 315; Kubas, G.J. Inorg. Chem. 1979, 18, 182; Ryan, R.R.; Kubas, G.J.; Moody, D.C.; Eller, P.G. Struct. Bonding (Berlin) 1981, 46, 47; Jarvinen, G.D.; Kubas, G.J.; Ryan, R.R. J. Chem. Soc. Chem. Commun. 1981, 385; Briant, C.E.; Hughes, G.R.; Minshall, P.C.; Mingos, D.M.P. J. Organomet. Chem. 1982, 224, C31; Briant, C.E.; Theobald, B.R.C.; Mingos, D.M.P. J. Chem. Soc. Chem. Commun. 1981, 963.

(7) McAuliffe, C.A.; Barratt, D.S.; Benson, G.G.; Venner, S.P. J. Chem. Soc. Dalton Trans., in press.

Figure Captions

Figure 1. The infrared spectra of a $Mn(PPhMe_2)Br_2$ film.: (a) following initial preparation; (b) following exposure to 50 Torr SO_2 for 24 hr at 298 K and then brief evacuation; (c) following an evacuation cycle for 12 hr at 10^{-6} Torr at 298 K; (d) following exposure to 120 Torr SO_2 for 72 hr at 298 K and lengthy evacuation.

Figure 2. The infrared spectra of a $Mn(PEt_3)Br_2$ film: (a) following initial preparation; (b) following exposure to 15 Torr SO_2 for 15 min at 298 K and then brief evacuation; (c) following an evacuation cycle for 24 hr at 10^{-6} Torr at 298 K; (d) following exposure to 50 Torr SO_2 for 24 hr at 298 K and then brief evacuation; (e) following evacuation for 24 hr at 10^{-6} Torr at 298 K. Band positions for analogous $S^{18}O_2$ complex spectra are given in parentheses.

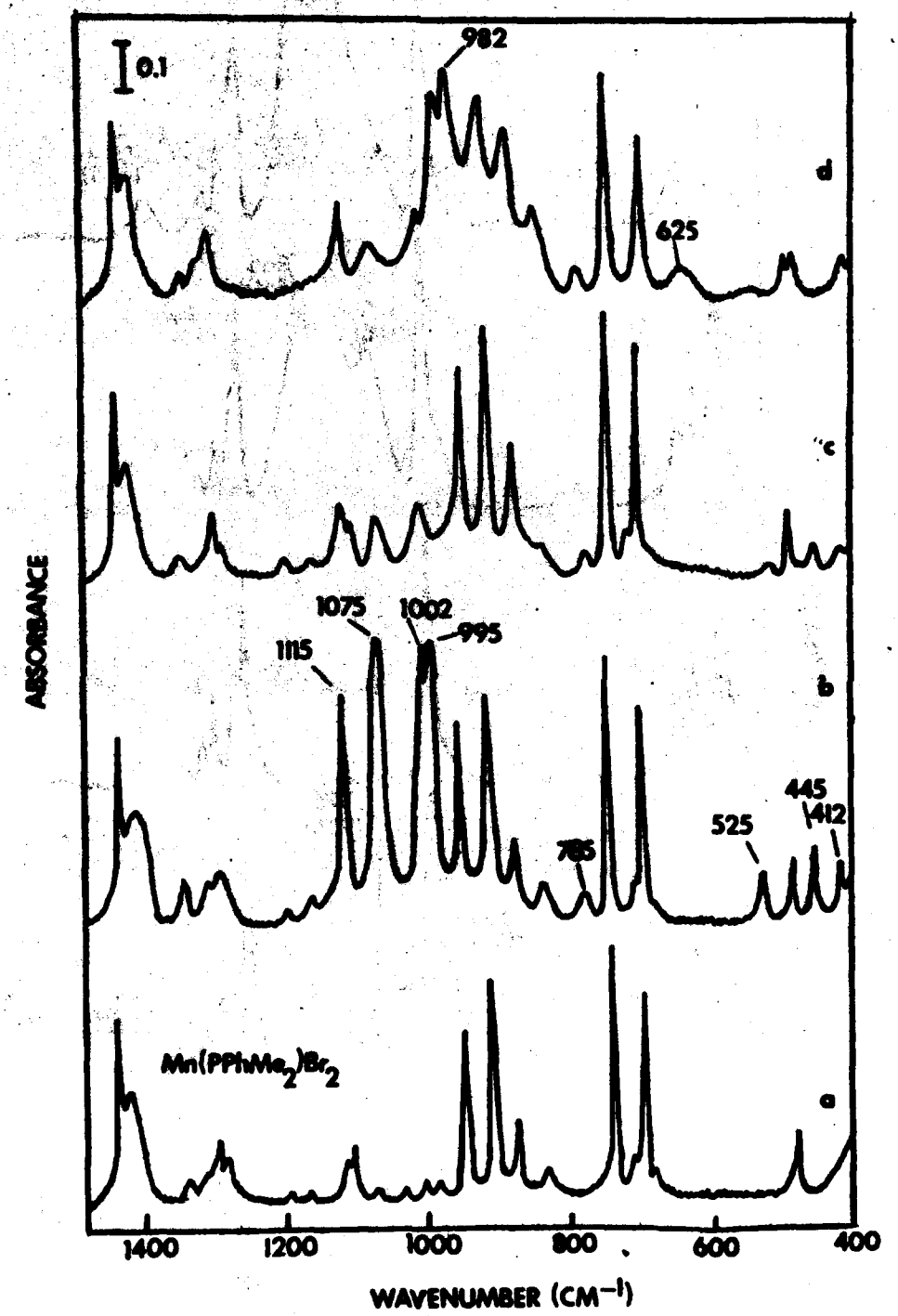
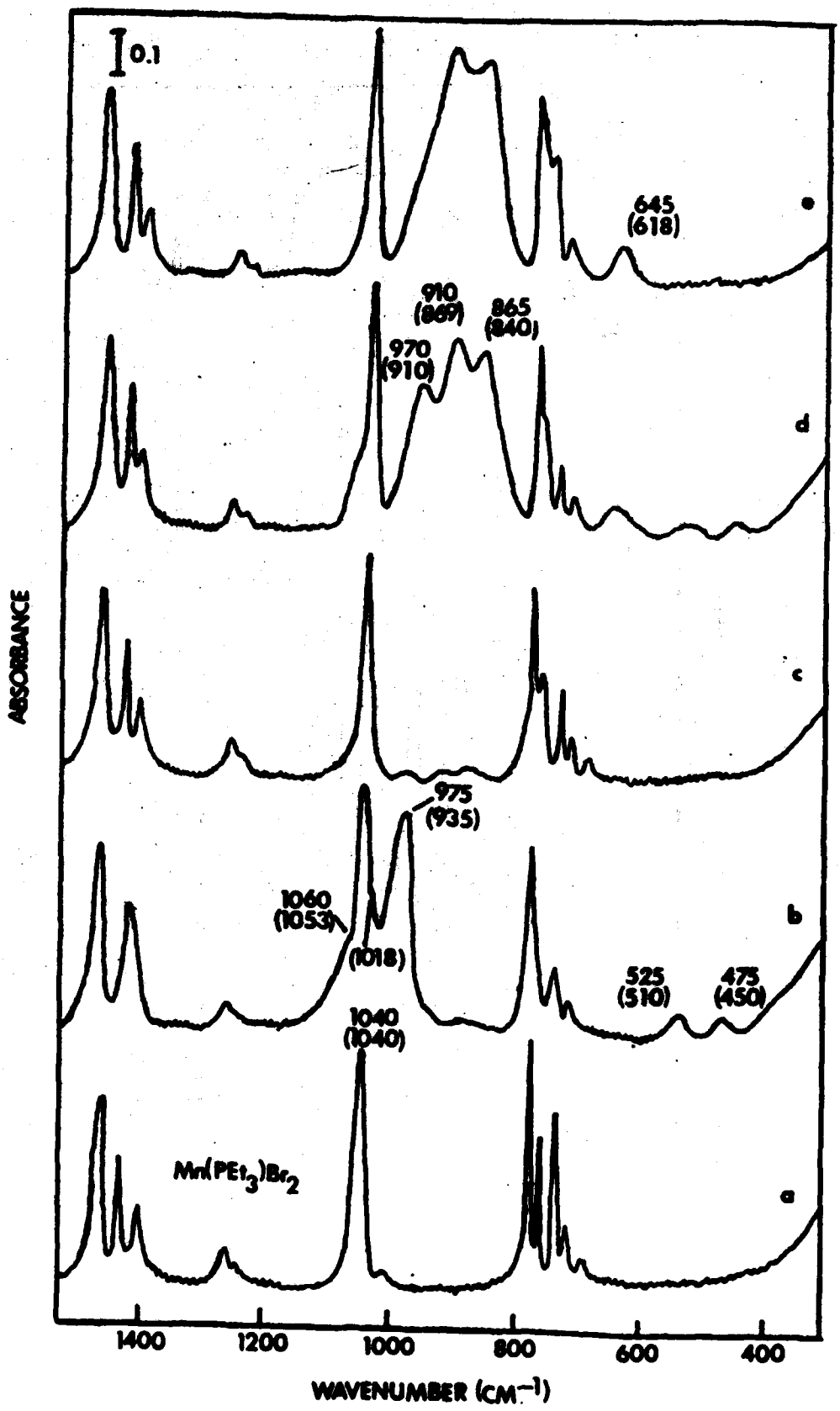

0.1
982
d
625
c
1075
1002
995
1115
b
445
525
412
785
Mn(PPhMe2)Br2
a
ABSORBANCE
1400
1200
1000
800
600
400
WAVENUMBER (CM⁻¹)

Fig. 1


0.1
645
(618)
e
910
(869)
865
(840)
970
(910)
d
c
975
(935)
1060
(1053)
(1018)
b
525
(510)
475
(450)
1040
(1040)
Mn(PEt3)Br2
a
ABSORBANCE
1400
1200
1000
800
600
400
WAVENUMBER (CM-1)

DL/413/83/01
GEN/413-2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1

	No. Copies
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

DTIC COPY INSPECTED 2

Accession For
NTIS GRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

DL/413/83/01
634/413-2

ABSTRACTS DISTRIBUTION LIST, 634

Dr. K. N. Nicholas
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019

Dr. Aaron Fletcher
Code 3852
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. J. Cooper
Code 6130
Naval Research Laboratory
Washington, D.C. 20375

Dr. M. C. Baird
Department of Chemistry
Queen's University
Kingston, Canada
K7L 3N6

Dr. N. N. Lichtin
Department of Chemistry
Boston University
685 Commonwealth Avenue
Boston, Massachusetts 02215

Dr. R. Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York 14627

Dr. N. Cooper
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Dr. S. D. Worley
Department of Chemistry
Auburn University
Auburn, Alabama 36830

Dr. L. Vaska
Department of Chemistry
Clarkson College
Potsdam, New York 13676

Dr. R. A. Huggins
Materials Science and
Engineering Department
Stanford University
Stanford, California 94305

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Auburn University		Office of Naval Research - Code 413
6c. ADDRESS (City, State and ZIP Code) Department of Chemistry (Dr. S.D. Worley) Auburn University Auburn University, AL 36849		7b. ADDRESS (City, State and ZIP Code) 800 N. Qunicy Street Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ONR	Code 413	N00014-83-K-0637
8c. ADDRESS (City, State and ZIP Code)		10. SOURCE OF FUNDING NOS.
See 7b		PROGRAM ELEMENT NO.: NR634-844 / PROJECT NO.: / TASK NO.: / WORK UNIT NO.:

11. TITLE (Include Security Classification) The Interaction of Complexes $Mn(PPhMe_2)Br_2$ and $Mn(PEt_3)Br_2$ With Sulfur Dioxide

12. PERSONAL AUTHOR(S)
W.E. Hill, S.D. Worley, D.K. Paul, and V.F. Newberry

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	85 Jul 18	8

16. SUPPLEMENTARY NOTATION
Accepted for publication in Inorg. Chem.

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	Infrared Spectroscopy, Manganese Complexes, Sulfur Dioxide

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The interactions of the complexes $Mn(PPhMe_2)Br_2$ and $Mn(PEt_3)Br_2$ as films with SO_2 and $S^{18}O_2$ have been investigated using infrared spectroscopy as an analytical probe. It is clear from these preliminary studies that two types of complexes with SO_2 have been formed. When the $MnLBr_2$ films were exposed to low pressures of SO_2 for relatively short times, an $MnLBr_2/SO_2$ complex formed reversibly in that the SO_2 could be removed by prolonged evacuation. On the other hand, lengthy exposure of the $MnLBr_2$ films to higher pressures of SO_2 caused the irreversible formation of a complex having stoichiometry $MnLBr_2 \cdot 1/2SO_2$. It is probable that the SO_2 bonds in some type of bridging fashion in both of the types of $MnLBr_2/SO_2$ complexes.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
S.D. Worley	(205)826-4043	

END

FILMED

9-85

DTIC