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INTERACTION OF $MnLX_2$ COMPLEXES WITH SULFUR DIOXIDE

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Complexes of stoichiometry $MnLX_2$ (L = tertiary phosphine, X = halogen) have been prepared as films on infrared windows. The complexes were exposed to SO_2 /evacuation cycles with their infrared spectra monitored before and after periods of exposure. For low pressure, relatively brief exposure times, a series of $MnLX_2/SO_2$ adducts were obtained which were reversible in that the SO_2 could be removed upon evacuation. However, a competitive decomposition channel existed, which was accentuated by longer exposures and higher pressure, which produced irreversible complexes having stoichiometry $MnLX_2 \cdot \frac{1}{2}SO_2$. Dioxygen was found to displace SO_2 from the reversible adducts, and SO_2 decomposed the dioxygen adducts to a mixture of the phosphine oxide complex and the irreversible SO_2 adduct. It has been postulated that SO_2 interacts with the polymeric $MnLX_2$ complexes through bridging coordination involving more than one of the atoms of SO_2 .

INTRODUCTION

McAuliffe and coworkers first reported the successful preparation and preliminary characterization of a broad series of manganese (II) complexes having stoichiometry $MnLX_2$ (L = tertiary phosphine, X = halogen) and proposed that the complexes mimicked myoglobin in their behavior with dioxygen.¹ Green and coworkers were not able to reproduce the work of McAuliffe and suggested that the dramatic color changes attributed by McAuliffe to $MnLX_2$ complexes reacting with dioxygen to form $MnLX_2 \cdot O_2$ complexes were due to a transient $Mn(III)$ species formed in an MnX_2/L system which ultimately decomposed by oxidation of the tertiary phosphine present.² McAuliffe later suggested that Green was unsuccessful possibly because of excess phosphine present and moisture contamination.³ Subsequently work in these laboratories⁴⁻⁶ and by King and coworkers⁷ and Wilkinson and collaborators⁸ established the existence of complexes of composition $MnLX_2$. Also complexes having composition MnL_2X_2 have been reported.⁹ We have developed a means by which complexes exhibiting similar properties to those reported by McAuliffe can be prepared as films on infrared windows under high-vacuum conditions ensuring that moisture and excess phosphine are not present at any time

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during the experiments when dioxygen or some other small molecule are exposed to the complexes.⁴⁻⁶ Using infrared spectroscopy we have shown the existence of the complexes and their interaction with dioxygen,^{4,5} and we have suggested that a colored complex of stoichiometry $\text{MnLX}_2 \cdot \text{O}_2$ does form in which Mn is in the (III) oxidation state (superoxide). We have demonstrated several cycles of reversibility in the interaction of MnLX_2 with dioxygen,^{4,5} but we have noted that the dioxygen complexes decompose in a competitive channel to the analogous phosphine oxide complexes $[\text{Mn}(\text{OPR}_3)_2\text{X}_2]$. The rates of the competitive reactions (dioxygen removal and decomposition to phosphine oxide complex) are markedly dependent upon the nature of the tertiary phosphine ligand employed.⁵

Recently McAuliffe and coworkers have reported that their bulk complexes in toluene solution or slurry react irreversibly with sulfur dioxide to give an adduct having stoichiometry $\text{MnLX}_2 \cdot 2/3\text{SO}_2$ with prominent infrared bands in the 1112–1140 cm^{-1} region.¹⁰ The purpose of this paper is to report infrared work from these laboratories concerning the interaction of SO_2 with the MnLX_2 films. A preliminary account of parts of this work has appeared.⁶

RESULTS

Infrared data and spectra for S^{16}O_2 and S^{18}O_2 interaction with the complexes $\text{Mn}(\text{PPhMe}_2)_2\text{Br}_2$ and $\text{Mn}(\text{PEt}_3)_2\text{Br}_2$ were presented in an earlier communication.⁶ For the complex $\text{Mn}(\text{PPhMe}_2)_2\text{Br}_2$, upon exposure to S^{16}O_2 (S^{18}O_2) at 50 Torr for 24 hr bands at 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 reaction of SO_2 with the $\text{Mn}(\text{PPhMe}_2)_2\text{Br}_2$. Several bands (including an intense one at 1115 cm^{-1} assigned to $\nu_{\text{PC-aryl}}$) which do not shift in cm^{-1} upon isotopic substitution can be assigned to ligand vibrational modes which are accentuated due to the presence of SO_2 . The bands at 995, 1002, and 1075 cm^{-1} do shift substantially upon isotopic substitution in SO_2 and must correspond to S—O stretching vibrational modes; the fact that three such bands were present indicates that more than one type of complex is possibly being formed. The bands at 412 and 445 cm^{-1} which shifted little upon isotopic substitution could correspond to Mn—S vibrational modes, while the band at 525 cm^{-1} which shifts to 515 cm^{-1} upon use of S^{18}O_2 probably corresponds to an Mn—O vibrational mode. Upon evacuation at 10^{-6} Torr for 12 hr all of the bands mentioned declined markedly in intensity; we have observed up to three cycles of exposure/evacuation before decomposition for this particular complex. Thus the initial complex formed between SO_2 and $\text{Mn}(\text{PPhMe}_2)_2\text{Br}_2$ is reversible. However, upon lengthy exposure (72 hr) at 120 Torr of SO_2 a new irreversible complex is formed containing prominent IR bands at 982 and 625 cm^{-1} which can not be attenuated by evacuation. Thus this complex behaves for SO_2 interaction in similar fashion to its behavior for dioxygen exposure, ie. it decomposes upon standing in contact with the gas under study. Bulk analysis of the final complex⁶ showed it to have stoichiometry $\text{Mn}(\text{PPhMe}_2)_2\text{Br}_2 \cdot \frac{1}{2}\text{SO}_2$.

Our early study of the interaction of $\text{Mn}(\text{PEt}_3)_2\text{Br}_2$ with S^{16}O_2 and S^{18}O_2 showed similar results, namely formation of a reversible SO_2 adduct which subsequently decomposes to a irreversible SO_2 adduct upon standing in the presence of SO_2 gas.⁶

In fact the reversible complex for Mn(PEt)₃Br₂ decomposes to the irreversible adduct even during prolonged evacuation, indicating that the presence of high pressures of SO₂ gas is not necessary to drive the decomposition channel for this complex.⁶ Bulk analysis of the irreversible adduct showed it to have stoichiometry Mn(PEt)₃Br₂ · $\frac{1}{2}$ SO₂.

The interactions of SO₂ with several other complexes of the form MnLX₂ (L = PPhMe₂, X = Cl, Br, I; L = PEt₃, X = Cl, Br, I; L = PMe₃, X = Cl, Br, I) have been studied here also. In general the results were analogous to those for Mn(PPhMe₂)Br₂ and Mn(PEt)₃Br₂. A reversible adduct was formed initially which could be cycled by SO₂ exposure/evacuation cycles. Subsequently each film decomposed to an irreversible adduct which was not affected by evacuation. A notable exception to this generalization was the complex Mn(PPhMe₂)Cl₂ which converted directly into the irreversible adduct upon exposure to 50 Torr of SO₂ for 24 hr (Figure 1). The infrared spectrum of this complex became broad and unresolved in the 800–1000 cm⁻¹ region and was not affected by prolonged evacuation. The SO₂ vibrational stretching modes for the various adducts have been presented in Table I. Again the 1118 cm⁻¹ band which is accentuated by the presence of SO₂ can be assigned to $\nu_{\text{PC-aryl}}$. All of the bulk analyses of the irreversible adducts studied indicated stoichiometry MnLX₂ · $\frac{1}{2}$ SO₂ (Table II).

A study of the reactions of dioxygen with the SO₂ adducts and SO₂ with the dioxygen adducts has been performed also. Figure 2 shows the spectral changes which occur for the reversible Mn(PPhMe₂)Br₂/SO₂ adduct (spectrum 2a) upon three exposures to dioxygen. The primary SO₂ adduct bands at 995, 1002, and

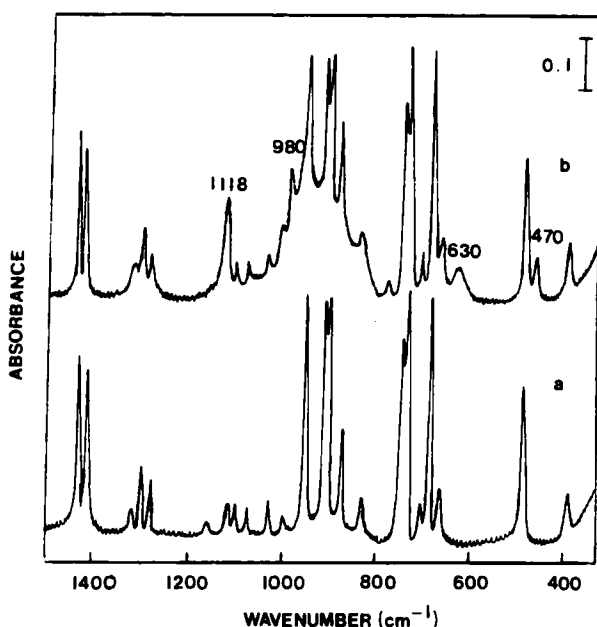


FIGURE 1 Infrared spectra corresponding to the interaction of a film of Mn(PPhMe₂)Cl₂ with SO₂: (a) unreacted complex at 10⁻⁶ Torr; (b) complex after exposure to 50 Torr of SO₂ for 24 hr followed by brief evacuation; prolonged evacuation at 10⁻⁶ Torr produced no further changes.

TABLE I
SO₂ stretching frequencies for a variety of MnLX₂/SO₂ complexes

Reversible Complexes	X	ν (cm ⁻¹)
Mn(PPhMe ₂)X ₂ /SO ₂	Br	1075, 1005–995
	I	1075, 1005
Mn(PEt ₃)X ₂ /SO ₂	Br	1060, 975
	Cl	1080, 975
	I	1057, 970
Mn(PMe ₃)X ₂ /SO ₂	Br	1055, 1010
	Cl	1068, 1005
	I	1050, 997
Irreversible Complexes	X	ν (cm ⁻¹)
Mn(PPhMe ₂)X ₂ · $\frac{1}{2}$ SO ₂	Br	982, 900–800
	Cl	980, 900–800
	I	1080–800
Mn(PEt ₃)X ₂ · $\frac{1}{2}$ SO ₂	Br	910, 865
	Cl	910, 875
	I	912, 875
Mn(PMe ₃)X ₂ · $\frac{1}{2}$ SO ₂	Br	910, 870–850
	Cl	910, 860
	I	906, 884

TABLE II
Elemental analyses of the irreversible sulfur dioxide complexes

Complex	% of element found (calculated)
Mn(PMe ₃)Br ₂ · 1/2SO ₂	C 10.9 (11.1), H 2.9 (2.8)
	Br 49.3 (49.5), S 4.9 (4.9)
	P 9.7 (9.6)
Mn(PMe ₃)I ₂ · 1/2SO ₂	C 8.5 (8.6), H 2.2 (2.2)
	I 60.8 (60.9), P 7.6 (7.4)
Mn(PEt ₃)Br ₂ · 1/2SO ₂	C 19.7 (19.7), H 4.2 (4.1)
	Br 43.7 (43.8), S 4.4 (4.4)
Mn(PPhMe ₂)Br ₂ · 1/2SO ₂	C 24.8 (24.9), H 3.0 (2.8)
	Br 41.4 (41.6), S 4.1 (4.2)

1075 cm⁻¹ decline markedly in intensity with the concomitant growth of a new band at 1140 cm⁻¹ attributable to the P—O stretching mode in the decomposition product Mn(OPhMe₂)Br₂.⁵ A band at 1360 cm⁻¹ also appeared following exposure to dioxygen. This band was removed upon brief evacuation and can thus be assigned to the antisymmetric stretching mode of gaseous SO₂.¹¹ Thus dioxygen clearly displaces SO₂ from the reversible adduct. Generally the dioxygen interaction with an MnLX₂ complex produces a deep color (blue for Mn(PPhMe₂)Br₂) which corresponds to a metastable superoxide species.⁵ No color was observed in this experiment indicating that the Mn(PPhMe₂)Br₂/SO₂ complex formed the phosphine oxide decomposition product Mn(OPhMe₂)Br₂ directly upon displacement of gaseous SO₂. This experiment was performed for the Mn(PPhMe₂)I₂/SO₂ complex also with analogous results.

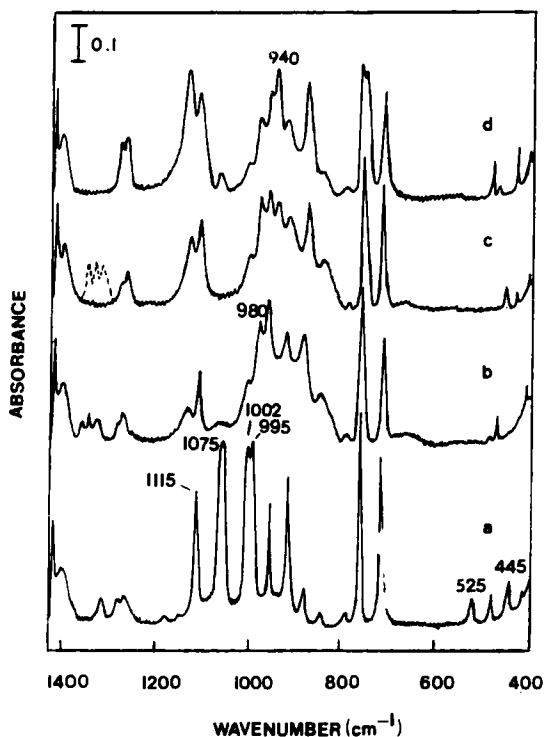


FIGURE 2 Infrared spectra corresponding to the interaction of a film of $\text{Mn}(\text{PPhMe}_2)\text{Br}_2$ with SO_2 and then O_2 ; (a) complex after exposure to 50 Torr SO_2 for 24 hr followed by brief evacuation; (b) following exposure to 100 Torr of O_2 for 30 min; (c) following exposure to 100 Torr of O_2 for 24 hr and brief evacuation (dotted curve shows $\text{SO}_2(\text{g})$ band before evacuation); (d) following exposure to 100 Torr of O_2 for 24 additional hr and evacuation for 30 min.

Previous experiments have shown that the complex $\text{Mn}(\text{PEt}_3)\text{Br}_2$ interacts reversibly with dioxygen to a greater extent than do the other complexes studied here.⁵ For this reason the $\text{Mn}(\text{PEt}_3)\text{Br}_2 \cdot \text{O}_2$ adduct was chosen for exposure to SO_2 gas. The results of this experiment are shown in Figure 3. Figure 3a presents the spectrum of the unreacted $\text{Mn}(\text{PEt}_3)\text{Br}_2$ complex film. After exposure to 200 Torr of dioxygen for 30 min, the complex became deep blue in color, and spectrum 3b was taken. The cell was then evacuated for 30 min and subsequently exposed to 8 Torr of SO_2 for 3 hr which produced spectrum 3c. At this point the film was white in color. Finally evacuation for 24 hr produced a surface giving spectrum 3d. Spectrum 3c indicates that a mixture of phosphine oxide decomposition product ($\text{Mn}(\text{OPEt}_3)\text{Br}_2$) and reversible $\text{Mn}(\text{PEt}_3)\text{Br}_2/\text{SO}_2$ adduct are being formed in this experiment. Spectrum 3d shows that evacuation removes the reversible adduct leaving the phosphine oxide complex and some irreversible $\text{Mn}(\text{PEt}_3)\text{Br}_2 \cdot \frac{1}{2}\text{SO}_2$. We were able to cycle this system twice (oxygenation/ SO_2 exposure/evacuation) before the system would no longer become colored, and the spectrum was that of the phosphine oxide complex and SO_2 irreversible adduct decomposition products exclusively. This experiment was repeated for the $\text{Mn}(\text{PEt}_3)\text{Cl}_2$ system with analogous results. We could find no infrared evidence for sulfate being produced in any of our experiments.

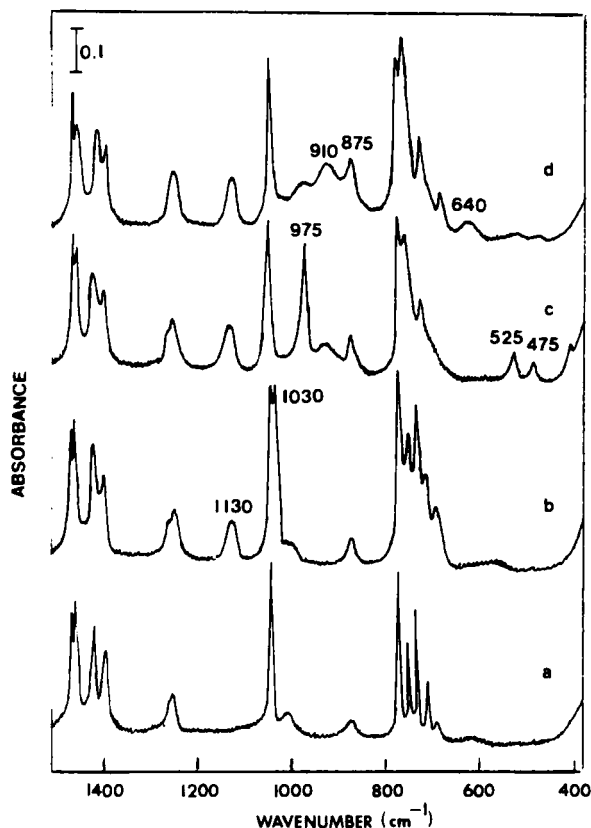


FIGURE 3 Infrared spectra corresponding to the interaction of a film of $\text{Mn}(\text{PEt}_3)\text{Br}_2$ with O_2 and then SO_2 ; (a) unreacted complex at 10^{-6} Torr; (b) following exposure to 200 Torr of O_2 for 30 min; (c) following evacuation for 30 min and exposure to 8 Torr of SO_2 for 3 hr and brief evacuation; (d) following additional evacuation at 10^{-6} Torr for 24 hr.

DISCUSSION

It is clear that two types of SO_2 adducts are formed in these experiments. As concerns the structures of these adducts, little can be said with confidence because there are little reliable data concerning the structure of the MnLX_2 complexes themselves. An X-ray crystal structure of the complex $\text{Mn}(\text{PPhMe}_2)_2\text{I}_2$ has been determined by King and coworkers.⁷ This structure showed the solid-state complex to be a polymeric array containing bridged halogens and manganese atoms alternating in tetrahedral/octahedral coordination with two phosphine moieties bonded to each octahedral Mn atom.⁷ We employed this crystal structure earlier in suggesting possible structures for the $\text{MnLX}_2 \cdot \text{O}_2$ and phosphine oxide decomposition products.⁵ However, we feel that it would not be useful to speculate in such an extensive manner at this time for the SO_2 adducts. Suffice it to say that our infrared data with SO_2 adduct bands in the $850\text{--}1080\text{ cm}^{-1}$ region would best describe a complex in which SO_2 exists in a bridging mode of coordination with more than one

of the SO₂ atoms coordinating (for a previous example, see the work of Kubas and coworkers¹² on [Mo(CO)₂(PPh₃)(Pyr)(μ-SO₂)]₂ · 2CH₂Cl₂).

Finally it should be noted that the stoichiometry for the irreversible adducts (MnLX₂ · $\frac{1}{2}$ SO₂) is different from that reported by McAuliffe and coworkers.¹⁰ Also they report no evidence of reversibility.¹⁰ However, their work was for MnLX₂ complexes in solution or slurry, and their method of preparation was considerably different from ours.

CONCLUSIONS

From this work it can be concluded that the MnLX₂ complexes do interact with sulfur dioxide. If SO₂ pressure is kept low (a few Torr), and exposure time is brief (a few hours), reversible SO₂ adducts are formed for most of the complexes. For longer exposure times, and even under prolonged evacuation, an irreversible decay channel exists which forms adducts of stoichiometry MnLX₂ · $\frac{1}{2}$ SO₂. The behavior of the MnLX₂ complexes upon interaction with SO₂ is thus similar to the behavior upon interaction with dioxygen except that the SO₂ adducts are not colored. We have noted that dioxygen displaces SO₂ from the reversible adducts and that SO₂ competitively decomposes the dioxygen adducts to the irreversible SO₂ adducts and phosphine oxide complexes. No infrared bands corresponding to sulfate species were obtained.

EXPERIMENTAL

The techniques used in preparing MnLX₂ complex films for infrared analyses have been described in detail elsewhere.⁵ Briefly a film of MnX₂ is deposited on a KBr infrared window by either sublimation of the anhydrous salt (X = Cl, Br) or spraying of a slurry of the salt in THF or MeOH onto a heated window (X = I). The films produced are then transferred to a specially designed IR cell⁵ and heated at 10⁻⁶ Torr at 493 K for 5–12 hr to remove all water and solvents. When a continuous base line in the infrared spectrum is obtained, the film is exposed to the vapor pressure of a dry tertiary phosphine through the vacuum system until suitable complex bands are obtained in the infrared spectrum (usually 0.5–2.0 hr). Then the film containing MnLX₂ and excess phosphine is evacuated at 10⁻⁶ Torr at ambient temperature until all excess phosphine is removed (as evidenced by no further change in the IR spectrum). Following this treatment, IR spectra are monitored before and after exposure to SO₂ or dioxygen. Perkin-Elmer Models 983 and 580 spectrometers with data systems were employed for this work. The gases S¹⁶O₂ and S¹⁸O₂ used in this work were obtained from Matheson Gas Products and Alfa Products, respectively, and used without further purification; the dioxygen employed was Matheson UHP. Manganese salts and phosphines were obtained from Cerac, Inc., and Strem Chemicals, Inc., respectively. The phosphines were subjected to distillation and repeated freeze/thaw evacuation cycles before use. The manganese salts were predried under heating and evacuation before sublimation or spraying.

The samples sent for bulk analyses (Atlantic Microlabs, Inc.) were prepared on a vacuum line also by expose of dry phosphine to dry MnX₂ powder in a tube which could be sealed. Evacuation at 10⁻⁶ Torr was used to remove all excess phosphine. Then the samples were exposed to 250 Torr of SO₂ for 120 hr, evacuated, stored under dry argon in the sealed tubes, and shipped for analyses. Samples were analyzed for C, H, X and S.

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