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The Interaction of Complexes Mn(PPhMe$_2$)Br$_2$ and Mn(PH$_3$)Br$_2$ with Sulfur Dioxide

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Abstract

The interactions of the complexes Mn(PPhMe$_2$)Br$_2$ and Mn(PH$_3$)Br$_2$ as films with $\text{SO}_2$ and $^{18}$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 $\text{SO}_2$ have been formed. When the MnLBr$_2$$_7$ films were exposed to low pressures of $\text{SO}_2$ for relatively short times, an MnLBr$_2$$_7$/SO$_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$$_7$ films to higher pressures of SO$_2$ caused the irreversible formation of a complex having stoichiometry MnLBr$_2$$_7$/12SO$_2$. It is probable that the SO$_2$ bonds in some type of bridging fashion in both of the types of MnLBr$_2$$_7$/SO$_2$ complexes.
There has been considerable recent interest in complexes of the form

\[ \text{MnL}_2 \] (L=tertiary phosphine, X-union) 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 \( \text{MnBr}_2 \)
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
\( \text{MnBr}_2 \) films were exposed to either DMFMe\(_2\) or Me\(_2\) in order to form the \( \text{MnL}_2 \)
complex films. Extensive evacuation at \(10^{-6}\) Torr was employed to remove all
traces of excess phosphine. The films thus prepared were exposed to
\( \text{SO}_2/\text{evacuation} \) cycles with infrared spectra (Perkin-Elmer Models 384 or 983
with data station) being monitored at appropriate intervals. Since \( \text{SO}_2(g) \)
exhibits infrared bands near 570, 1150, and 1360 cm\(^{-1}\) which might have
interfered with resolution of the complex bands, the cell was always briefly
evacuated following \( \text{SO}_2 \) exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the \( \text{Mn(DMFMe}_2\)Br}_2 \)
complex film interacting with \( \text{SO}_2 \). A comparison of Fig. 1b and la reveals
that new infrared bands at \( \text{SO}_2(g^{18} \text{O}_2) \): 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 \( \text{SO}_2 \) with
ing major band at 3832 cm⁻¹ do to which does not shift
investigated and the monochromator was set at a 60 cm⁻¹
(3869 cm⁻¹), which is assigned due to the presence of 308; this band was
also present, but it increased in the presence of dimethyl. All of the bands
were present and also partially gone evacuation at 10⁻⁶ Torr for 12 hr
(Ref. 10). We were able to observe cycling of the intensities of these
bands upon exposure/exposure for up to three cycles; eg. 12 hr evacuation
in vacuum as essentially removes the SO₂. However, upon lengthy exposure
(72 hr) at high pressure (120 Torr) spectrum 16 resulted which could not be
prepared by lengthy evacuation. The bands at 808, 1002, and 1075 cm⁻¹ for
the complex were not particularly stable, in some and obviously correspond
to the generation of internal modes; the fact that three such bands were
present, indicates that more than one type of complex is probably being
generated. The remaining bands at 612 and 840 cm⁻¹ shifted little
(10 cm⁻¹) and (10 cm⁻¹), these bands could correspond to O=O=O modes. The
bands at 3869, 3475, 1410, and 557 cm⁻¹ in 16 did shift appreciably when SO₂
was replaced with 18O₂ (14, 16).

14. Figure 4 shows a detailed analysis of experiments for SO₂/Na₂MoO₄
interest in with SO₂. Band positions for SO₂ complex species 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 Na₂MoO₄/SO₂
complexes were formed in these experiments - one in which the SO₂ binds
reversibly and one in which the SO₂ is coordinated in an irreversible
fashion. Comparison of the intensities of the 865, 910, and 970 cm⁻¹ bands
in spectra 14 and 16 reveals that the reversible complex can decompose to
the irreversible one even during evacuation following high SO₂ exposures.
Comparisons of the two thermal decomposition step complexes were prepared 
and the results of IR spectra were consistent with the original 
comparison conditions. The silver analysis of the two 
complex decomposition step complexes revealed that the activity of 
water for each step was different. This was also evident from the 
observation of infrared bands in the 600-100 cm⁻¹ region of the spectra 
that the two forms of each complex contains 10⁻⁷ mol added in a bridging site, with more 
than mononuclear or bimetallic involving in the bridge. Final structure determination 
must await x-ray crystallographic data.

It should be noted that McMillan and coworkers have reported recently 
the reaction of Mg with several ligand complexes in solution and in 
solution reactions. They report a stability of Mg²⁺/Mg³⁺ for their 
solution studies, and they were not able to observe reversibility. 
Furthermore, they report absorption features between 870-1000 cm⁻¹ 
which are not observed for the Mg₃[Co₂(C₄H₆N₃)₆] complex film. However, 
their experimental conditions (liquid phase, 760°C for 15 minutes) were quite 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.

Acknowledgments

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Corporation, and the Auburn University Energy Grant-In-Aid program for 
partial support of this work. They also thank C.A. McMillan for a preprint 
of reference 7.


(5) Anal. Calcd (Atlantic Microlabs, Inc.) for Mn(PPhMe2)Br2·1/2SO2:
   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(PPh3)Br2·1/2SO2:


**Figure Captions**

**Figure 1.** The infrared spectra of a Mn(PFMe₂)Br₂ film:
(a) following initial preparation; (b) following exposure to 50 Torr SO₂ 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 SO₂ for 72 hr at 298 K and lengthy evacuation.

**Figure 2.** The infrared spectra of a Mn(PEt₃)Br₂ film: (a) following initial preparation; (b) following exposure to 15 Torr SO₂ 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 SO₂ 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 §¹⁸O₂ complex spectra are given in parentheses.
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