terms of their inductive effect on the phen π-electron system.

The visible absorption and emission spectra of the tris complex, Ru(BDCMP)$_3^{4-}$, are the most red shifted compared to the other complexes in this study. Two well-separated absorption bands are observed for this complex (Table II; Figure 3), one of which (381 nm) is relatively narrow and resembles closely in shape, intensity, and energy the main visible absorption band of the free ligand at ~400 nm. On the basis of prior studies of dicyanomethylene-substituted organic dye systems,[33] this band can be reasonably attributed to a basically ligand-centered transition, in which negative charge is transferred from the nitrogen atoms to the dicyanomethylene groups.

The extremely broad absorption band at lower energies (502 nm) has no obvious counterpart in the spectrum of the free ligand and probably rises from MLCT; however, the complex shape and broad character of this band suggest that it is comprised of several transitions, the precise nature of which is impossible to determine on the basis of the data currently available. The relatively long lifetime of the corresponding emission at >700 nm is, at least, consistent with expectations for a MLCT excited state for this system.

Efforts to determine the redox properties of this complex were frustrated by the totally irreproducible character of the cyclic voltammograms obtained. Both oxidation and reduction features were observed in the several potential scans made, but their occurrence and position depended on the range of potentials scanned and no reversible or even reproducible features could be characterized even after repetitive cycling within the same potential limits. In addition to an apparent instability toward electrochemical oxidation or reduction, this complex also exhibits an unusual sensitivity toward oxygen under certain conditions. Solutions of this complex in acetonitrile, when maintained in an inert atmosphere, can be exposed to room light without apparent change; moreover, they also seem to be unaffected by exposure to air or oxygen if room light is excluded. On the other hand, exposure to both air and light produces an irreversible change in the color of these solutions from red-violet to orange-red, and in the absorption spectrum the broad band at 502 nm is replaced by an absorption at around 460 nm. Similar changes were observed in other solvents, including water, acetone, ethanol, and dichloromethane. Attempts to reverse this reaction by removal of the oxygen or the addition of a reducing agent (thiosulfate) did not prove successful. Further studies of this photoreaction with oxygen, including the identification of the photoproducts, were not attempted.

In the absence of oxygen, this complex is indefinitely stable in both aqueous and nonaqueous solution and can be recovered from these solutions on addition of a nonsolvent or evaporation. It absorbs more strongly in the visible region than the Ru(bpy)$_3^{2+}$ system (Table III) and has an energetic excited state whose lifetime is even longer than that of Ru(bpy)$_3^{2+}$. As such, it is a worthy subject for further investigation of photochemical electron-transfer processes as well as for possible use in photochemical energy conversion processes that do not require exposure to oxygen.

Acknowledgment. M.N.A. thanks Oberlin College for a sabbatical leave during which most of this work was completed and the National Science Foundation, through a Science Faculty Professional Development Award, and the General Electric Company for financial support. The authors also thank Drs. D. Cluxton, Russell Sage College, and E. E. Uzgiris, GE CRD, for the use of their apparatus and expertise for the measurement of the luminescent lifetimes and Professor M. Wrighton, MIT, for valuable discussions and preliminary evaluation of the Ru(phen)$_{3-x}$(Cl$_2$phen)$_x^{2+}$ complexes as a potential source of electroactive polymeric films.

Registry No. (9-PDP)ZnCl$_3$, 92543-36-7; Ru(phen)$_2$(Cl$_2$phen)(AsF$_6$)$_2$, 92543-38-9; Ru(phen)$_2$(Cl$_2$phen)Cl$_2$, 92543-39-0; Ru(phen)$_2$Cl$_2$, 85718-09-8; Ru(Cl$_2$phen)$_3$(AsF$_6$)$_2$, 92543-41-4; Ru(Cl$_2$phen)$_3$Cl$_2$, 23757-38-2; Ru(phen)$_2$(9-PDP)(ClO$_4$)$_3$, 92575-07-0; Ru(DP)$_3$(AsF$_6$)$_2$, 92543-43-6; Ru(DP)$_3$(ClO$_4$)$_2$, 92543-44-7; Ru(phen)$_2$(BDCMP), 92543-45-8; [(C$_6$H$_5$)$_3$PCH$_3$]$_4$[Ru(BDCMP)$_3$], 92575-09-2; [Ru(phen)$_2$(BDCMPH$_2$)]$^{2+}$, 92543-46-9; malononitrile, 109-77-3.

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Interaction of Complexes of Composition MnLX$_2$ (L = Tertiary Phosphine) with Dioxygen

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The complexes MnBr$_2$PMe$_3$, MnBr$_2$PEt$_3$, and MnBr$_2$PPhMe$_2$ have been prepared as films on infrared windows under completely anhydrous conditions with care being taken to eliminate all free phosphine. These films have been exposed to dioxygenation/evacuation cycles in a specially designed infrared cell with infrared spectra being monitored under carefully controlled conditions. This work has indicated that such complexes do exist in solid-state films and do interact with dioxygen. However, the extent of the reversibility of the interaction with dioxygen is markedly dependent upon the nature of the tertiary phosphine ligand employed. All of the solid-state complexes studied in this work exhibit an irreversible decay channel in the presence of dioxygen to a phosphine oxide complex decomposition product at ambient temperature.

Introduction

There exists a lively controversy at the present time concerning the existence of complexes of composition MnLX$_2$ (L = tertiary phosphine, X = anion) and their interaction with dioxygen. McAuliffe and co-workers first reported the preparation and characterization of a broad series of the manganese(II) complexes and suggested that the complexes mimicked myoglobin in their behavior with dioxygen.[1] Green

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and co-workers have subsequently cast doubt on the work of McAuliffe; they were not able to prepare complexes of composition $MnLX_2$ that reversibly interacted with dioxygen.[2] In fact they 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 that ultimately decomposed by oxidizing the tertiary phosphine present.[2] McAuliffe has rebutted the arguments of Green and co-workers by emphasizing the need for preparing the $MnLX_2$ complexes under "absolutely anhydrous conditions" and by ensuring that excess phosphine is not present during the dioxygen uptake experiments.[3] Recently, crystal structures of similar $MnLX_2$ complexes[4] and of $Mn(PPhMe_2)I_2$[5] have been reported. In these laboratories considerable effort has been expended during the past 3 years in an attempt to answer some of the questions raised concerning the existence of the $MnLX_2$ complexes and the nature of the interaction of the complexes, if they do exist, with dioxygen. The primary analytical probe used in these studies has been infrared spectroscopy.

Our first attempt at preparing the $MnLX_2$ complexes for infrared analyses generally followed the procedures reported by McAuliffe.[1] We were able to produce complexes that did uptake dioxygen accompanied by marked color changes, that did lose their color upon evacuation, that did exhibit these color changes upon several cycles of oxygenation/evacuation at room temperature, and that did provide elemental analyses in reasonable accord with the formula $MnLX_2$. However, all attempts to prepare pellets for infrared analysis under inert, anhydrous conditions provided samples that exhibited infrared bands near 3500–3450, 1600, and 550 cm^{-1} indicative of moisture contamination. These samples did uptake dioxygen (not quantitative) and change color reversibly, but any cycling of infrared band intensities upon oxygenation/deoxygenation cycles seemed to be related to the intensities of the "water bands" such that definitive conclusions could not be advanced. Also, it was apparent that all infrared samples prepared in this manner were slowly decomposing to phosphine oxide and/or an $MnL'X_2$ (L′ = phosphine oxide) complex because intense infrared bands at ca. 1150 cm^{-1} grew with time. Ultimately the phosphine oxide complexes were not active in dioxygen uptake and did not undergo color change. Recently McAuliffe and co-workers have reported a similar decomposition process for the complexes in solution when in the presence of high-pressure dioxygen and/or ambient temperature; however, they report numerous reversible cycles of dioxygen uptake and release at low temperature and pressure.[6]

A new technique for preparing the complexes for infrared analysis has been developed here recently which ensures that the complexes are free of moisture and excess phosphine contamination. In this procedure MnX_2 is carefully sublimed or sprayed as a THF or alcohol slurry onto a KBr infrared window. The film of MnX_2 produced is then heated under evacuation in an infrared cell to liberate all water. The dry film is exposed to dry tertiary phosphine vapor generally at room temperature through the vacuum system, which produces an anhydrous $MnLX_2$ film. Lengthy evacuation (ca. 10^{-6} torr) is employed to remove all traces of excess phosphine. The sample can then be subjected to dry dioxygenation/evacuation cycles, and infrared analysis can be performed with no chance of moisture contamination. A preliminary communication describing the infrared analyses of $MnBr_2PMe_3$ and $MnBr_2PMe_3{\cdot}O_2$ films has appeared recently.[7] The purposes of this paper are to describe our studies of $MnBr_2PMe_3$ in more detail and to present recent data concerning the complexes $MnBr_2PEt_3$ and $MnBr_2PPhMe_2$.

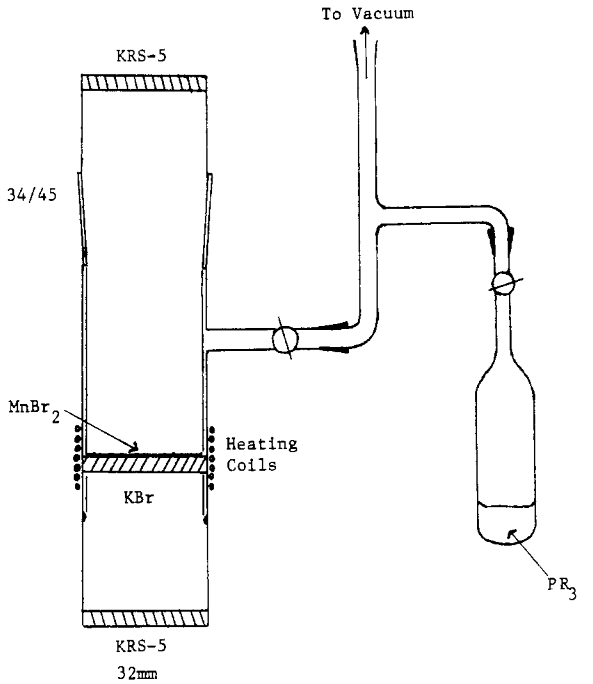

Figure 1. A typical Pyrex infrared cell employed in this work.

Experimental Section

Manganese(II) bromide (Cerac, Inc.) that is preheated to 673 K under vacuum for 6 h and handled in a drybox is sublimed onto a KBr infrared window mounted in a sublimator designed in these laboratories. This is accomplished by slowly raising the temperature of the sublimator over a 2-h period to ca. 823 K. This temperature is then maintained for a period of 30–90 min depending upon the thickness of $MnBr_2$ film desired. The KBr window containing the $MnBr_2$ film is then transferred in a drybox to one of several infrared cells designed in these laboratories (e.g. Figure 1). It should be noted that the $MnBr_2$ film can also be prepared by spraying a slurry of $MnBr_2$/(THF or MeOH) onto a heated KBr window (less than 373 K); evaporation of the solvent leaves the $MnBr_2$ film. The spectroscopic properties of the $MnBr_2PMe_3$ complex prepared from the $MnBr_2$ deposited by either method are the same, indicating minimal structural change of $MnBr_2$ caused by sublimation.

The $MnBr_2$ film in the infrared cell is heated under vacuum to ca. 493 K at 10^{-6} torr for sufficient time (usually 5–12 h) to remove all water. When a continuous base line in the infrared spectrum is obtained, the film is exposed through the grease-free vacuum system to a tertiary phosphine at its vapor pressure for 30 min ($PPhMe_2$) or 2 h (PEt_3) or at 400 torr for 45 min (PMe_3). The phosphines (Strem Chemicals, Inc.) are distilled and subjected to repeated freeze/thaw evacuation cycles before use. The film containing $MnBr_2PR_3$ is then subjected to evacuation at 10^{-6} torr for 4–12 h at room temperature to remove all traces of excess phosphine. Following this treatment

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infrared spectra (Perkin-Elmer Model 580 or Model 983 with data station) are monitored before and after exposure to dioxygen ($^{16}O_2$, Mathesen UHP; $^{18}O_2$, Alfa), evacuation, etc.

Results and Discussion

The Trimethylphosphine Complex of $MnBr_2$. The infrared spectra of films of $MnBr_2$, $MnBr_2PMe_3$, $MnBr_2PMe_3{\cdot}O_2$, and $MnBr_2OPMe_3$ and of the ligands PMe_3 (gas) and $OPMe_3$ (solid film) were presented in an earlier communication.[7] The spectra for PMe_3 and an $MnBr_2$ film exposed to PMe_3 were substantially different in terms of band frequencies and relative band intensities, indicating that a complex had formed. The same was true for the spectrum of $OPMe_3$ as compared to that of a $MnBr_2$ film exposed to $OPMe_3$. To provide substantiating evidence for the existence of the $MnBr_2PMe_3$ complex, the suspected complex film was exposed to dioxygen at a pressure of 400 torr and a temperature of 523 K for 2 h until all of the blue color disappeared, and the infrared spectrum became almost identical with that of the $MnBr_2/OPMe_3$ film. At this high temperature a band near 1150 cm^{-1} for free $OPMe_3$ sublimed from the film was also observed. The stoichiometry of the phosphine oxide complex was determined by preparing a sample in a sealed tube under the same conditions; an elemental analysis of this sample showed the stoichiometry to be $MnBr_2OPMe_3$.[7,8] Recently in these laboratories it has been shown by infrared that an $MnCl_2/PMe_3$ film converts to $MnCl_2OPMe_3$ upon standing in the presence of dioxygen at a pressure of 100 torr at room temperature for 10 days with no decomposition to free $OPMe_3$. These observations can only rationally be explained by the existence of the complex MnX_2PMe_3 upon exposure of MnX_2 to free PMe_3. Thus we do support the claims of McAuliffe concerning the existence of MnX_2PR_3 complexes, at least as regards solid-state films.

The earlier work in these laboratories[7] established that, upon exposure of an $MnBr_2PMe_3$ film to $^{16}O_2$ at a pressure of 100 torr at room temperature for 5 h, new infrared bands at 1132, 1060, 865, 570, and 409 cm^{-1} become evident (see Figure 2 in ref 7). All of these bands occur at lower frequency (1095, 1040, 860, 545, and 395 cm^{-1}) if an identical sample is exposed to $^{18}O_2$, indicating that at least one oxygen atom is involved in all of the vibrational modes represented. The bands at 865 and 409 cm^{-1} initially are weak but grow in intensity with time of exposure to dioxygen and are present (862, 400 cm^{-1}) also in the spectrum of the authentic $MnBr_2OPMe_3$ complex, so it can be assumed that these bands may be assigned to the oxide complex, which is the final decomposition product. An intense band near 1130 cm^{-1} also occurs for the phosphine oxide complex. However, we believe that the initial band at 1132 cm^{-1} that is evident for the film during the initial stages of dioxygenation while it is dark blue must refer at least in part to a vibrational mode for the oxygenated complex $MnBr_2PMe_3{\cdot}O_2$. This band decayed in intensity and broadened concomitantly with the band at 570 cm^{-1} upon increased exposure time to dioxygen. Finally when the color of the film disappeared, the 570-cm^{-1} band vanished, and the 1132 cm^{-1} band became very broad and weak. A band at 1130 cm^{-1} grows in again as the final phosphine oxide decomposition product (white) is formed as the predominant species. For dioxygen complexes, an infrared band in the 1100–1200-cm^{-1} region is indicative of an O–O stretching mode for a dioxygen species bonded in an end-on, bent configuration.[9-13] We believe that the dioxygen is present as a superoxide species with Mn in the III oxidation state providing the chromophore. This postulate is in accord with one of the conclusions of Green and co-workers, but it should be emphasized that we are considering specifically the solid-state $MnBr_2PMe_3$ film. It is possible that other oxygenated MnX_2PR_3 complexes and MnX_2PR_3 complexes in solution in general may not involve a superoxide species or that the oxygenated complexes of McAuliffe prepared differently from ours may have different structures. It should be noted that a superoxide manganese phthalocyanine dioxygen adduct has also been reported recently.[13] The 570-cm^{-1} band for $MnBr_2PMe_3{\cdot}O_2$, which is broad and has rather low intensity, could then be assigned to the Mn–O stretching mode in the transient superoxide species.

The 1060-cm^{-1} band for the $MnBr_2PMe_3{\cdot}O_2$ complex grows steadily with exposure time to dioxygen but does not vanish when the complex finally loses its blue color. Ultimately the 1060-cm^{-1} band does decline in intensity with a concomitant growth of the oxide band at 1130 cm^{-1}. This indicates that a second transient intermediate is being formed along the decomposition reaction pathway to $MnBr_2OPMe_3$. Work in these laboratories concerning the reaction of gas-phase PMe_3 and O_2 has shown that a similar infrared band near 1060 cm^{-1}, which is not present in the infrared spectrum for $OPMe_3$, occurs.[14] For the gas-phase reaction this band can be assigned to PMe_2OMe (the infrared spectrum of PMe_2OMe contains a strong band at 1068 cm^{-1}).[15] Thus we attribute the band at 1060 cm^{-1} for the $MnBr_2PMe_3{\cdot}O_2$ complex to an alkoxyphosphine complex, which subsequently isomerizes to the phosphine oxide final decomposition product. This process occurs slowly for the complex at room temperature but can be expedited by heating in the presence of dioxygen (400 torr) at 583 K for 13 h. It should be noted that heating a $MnBr_2PMe_3{\cdot}O_2$ film in the presence of dioxygen causes the formation of a new infrared band at 1040 cm^{-1} as well as the feature at 1130 cm^{-1}. The final $MnBr_2OPMe_3$ complex does not exhibit this band at 1040 cm^{-1}, so presumably is signifies another decomposition intermediate, possibly a dialkoxyphosphine complex or a $MnBr_2OPMe_2OMe$ complex (the infrared spectrum of free $OPMe_2OMe$ gives a prominent band at 1044 cm^{-1}).[16]

Another controversial point concerning $MnBr_2PR_3$ interaction with dioxygen is whether or not the interaction process is reversible. For the case of the $MnBr_2PMe_3$ film we can see little evidence of a reversible interaction. Extensive evacuation at room temperature does not cause significant decline of the superoxide infrared bands nor loss of the intense blue color. When the color finally does disappear upon heating or in the presence of high pressures of dioxygen, the $MnBr_2PMe_3{\cdot}O_2$ film has been converted into decomposition products (alkoxyphosphine and phosphine oxide complexes). We have not studied the behavior of the $MnBr_2PMe_3$ complex in solution or at low temperature and pressure.

It should be noted that McAuliffe and co-workers have recently questioned our early work concerning the interaction of $MnBr_2PMe_3$ with dioxygen and the subsequent decomposition of the superoxide species to the $MnBr_2OPMe_3$ complex.[17] They exposed a sample of solid-state MnI_2PMe_3 to dioxygen

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(8) Anal. Calcd (Atlantic Microlab, Inc.) for $MnBr_2OPMe_3$: C, 11.74; H, 2.96; Br, 52.08. Found: C, 11.81; H, 2.96; Br, 51.99.

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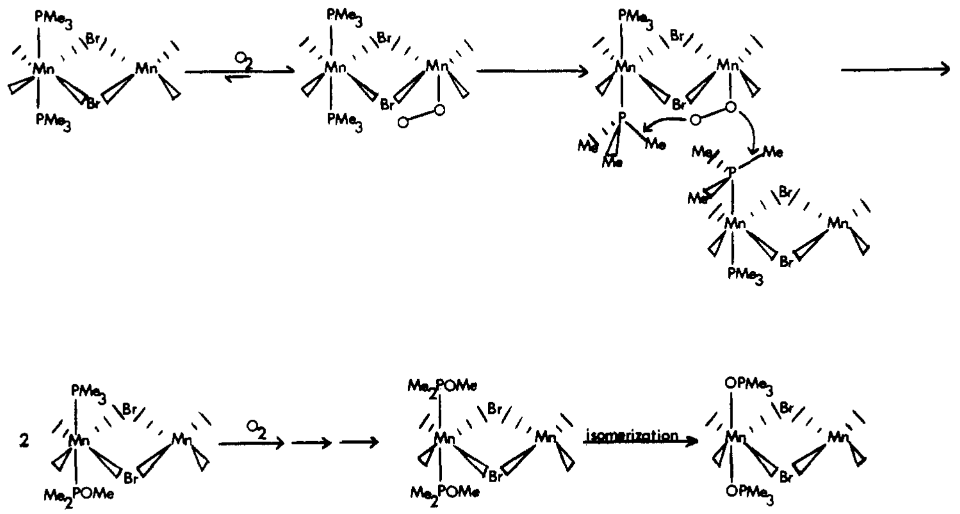

Figure 2. Reaction scheme for the interaction of dioxygen with the $MnBr_2PMe_3$ complex (see text).

and vacuum sublimed the resulting dark green solid onto a cold finger, leaving a "flesh-colored residue which contained Mn and I, but no C or P". An X-ray crystal structure was performed on the "dark green" crystals from the cold finger, which revealed the material to be $MnI_3(PMe_3)_2$ and led the authors to suggest that $MnBr_2PMe_3{\cdot}O_2$ and $MnBr_2OPMe_3$ are not formed in the oxygenation of $MnBr_2PMe_3$. To test this conclusion, we have recently exposed anhydrous $MnBr_2$ to PMe_3 in our vacuum sublimator, evacuated excess phosphine for 6 h, and exposed the resulting solid material to dry dioxygen at 150 torr for 30 min and then 300 torr for 30 min at ambient temperatures. Following subsequent evacuation, the resulting purple/blue solid was vacuum sublimed onto a KBr infrared window; this sublimation was accomplished in the range 623–633 K, and the crystals produced in the sublimate were white. The infrared window was transferred to an IR cell in a drybox. The resulting infrared spectrum contained the usual prominent bands at ca. 1125, 1080, and 1055 cm^{-1} characteristic of oxygenated $MnBr_2PMe_3$ in an advanced state of decomposition (to $MnBr_2OPMe_3$ and its inactive precursor—see next paragraph). We have produced essentially the same results using $MnI_2PMe_3{\cdot}O_2$ at a lower sublimation temperature (548 K). Thus it would appear that the $MnBr_2PMe_3{\cdot}O_2$ complex was produced as a film in these laboratories and that care should be exercised when one attempts to sublime oxygenated complexes to minimize decomposition.

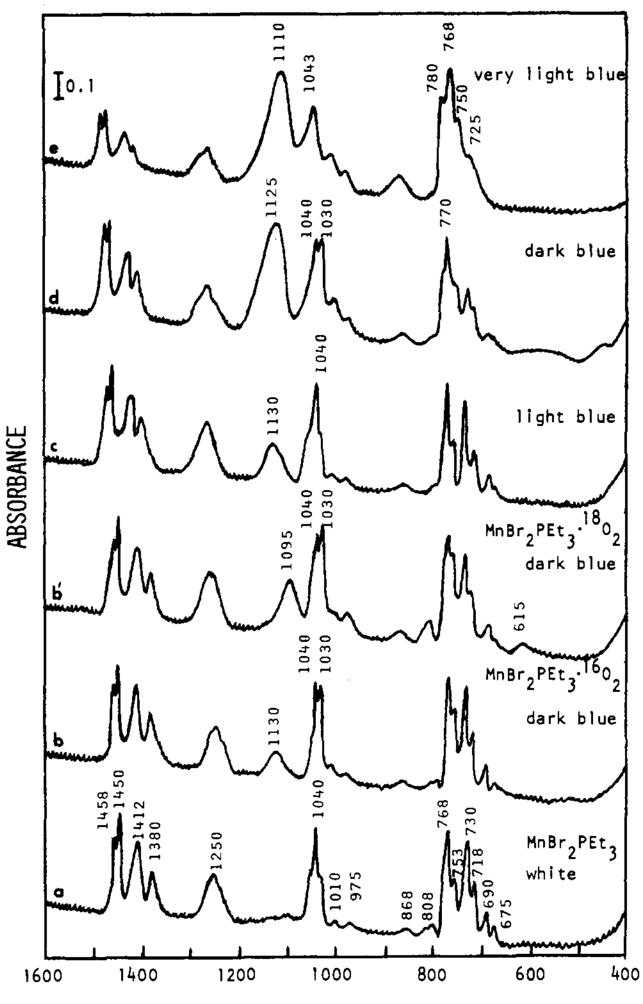

Figure 3. Infrared spectra of $MnBr_2PEt_3$, $MnBr_2PEt_3{\cdot}O_2$, and $MnBr_2OPEt_3$: (a) complex film prepared as described in the text; (b) following exposure to 88 torr of $^{16}O_2$ for 60 min and then 246 torr of $^{16}O_2$ for 40 min; (b′) a second complex film following exposure to 200 torr of $^{18}O_2$ for 90 min; (c) film from (b) evacuated at ca. 10^{-6} torr for 20 h at room temperature; (d) further exposure of film from (c) to 280 torr of $^{16}O_2$ for 90 min (blue), followed by evacuation for 18 h (white), followed by exposure to 230 torr of $^{16}O_2$ for 4 h; (e) further exposure of film from (d) to 550 torr of $^{16}O_2$ for 24 h.

A speculative reaction scheme that is consistent with the facts that have been accumulated for the $MnBr_2PMe_3$ complex is shown in Figure 2. An X-ray crystal structure of the complex MnI_2PPhMe_2 has been determined by King and collaborators.[5] This structure shows the solid-state complex to be a polymeric array containing bridged halogens and manganese atoms alternating in tetrahedral/octahedral coordination. Two phosphine moieties are bonded to each octahedral manganese atom. Since there is no crystal structure available for any of the complexes studied in this work, we have chosen to use the King structure as a basis for our proposed speculative reaction scheme for $MnBr_2PMe_3$ in Figure 2. Our infrared evidence indicates that a transient superoxide species forms first; it is reasonable to assume that the dioxygen moiety would be bonded end-on to a tetrahedral manganese site. Decomposition could proceed by insertion of the two oxygen atoms into P–C bonds, possibly for phosphine moieties in different layers as indicated in the figure, to form an alkoxyphosphine complex. The process could then be repeated to form a complex having two alkoxyphosphine moieties. Finally, isomerization would give the final phosphine oxide complex having the correct stoichiometry. Of course, other speculative reaction schemes could be written that might ra-

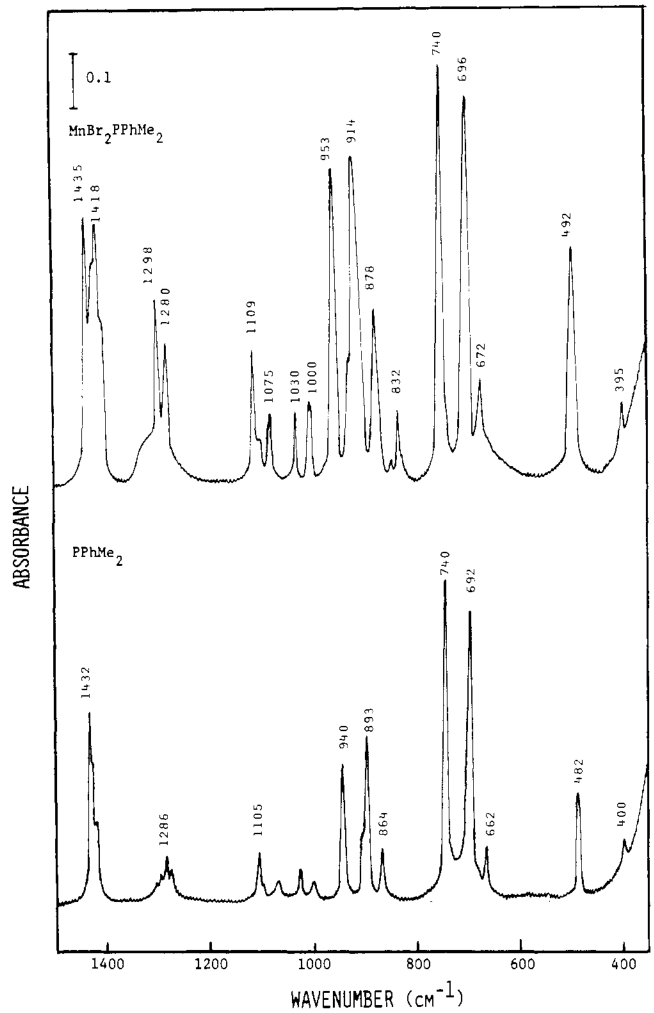

Figure 4. Infrared spectra of a liquid film of $PPhMe_2$ on a KBr window and a film of $MnBr_2$ exposed to $PPhMe_2$ as discussed in the text.

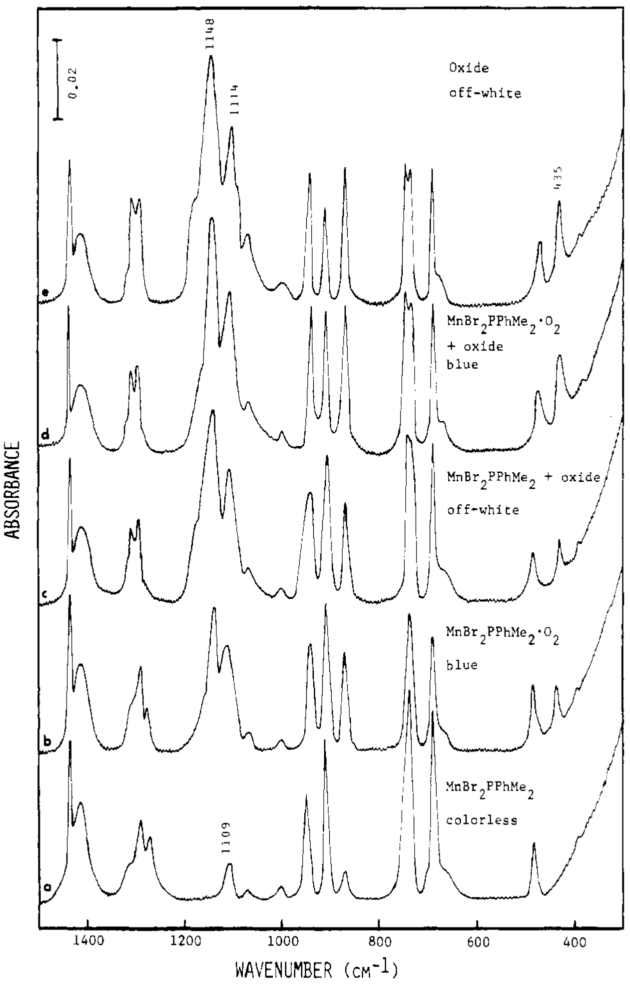

Figure 5. Infrared spectra of $MnBr_2PPhMe_2$, $MnBr_2PPhMe_2\cdot{}^{16}O_2$, and $MnBr_2{}^{16}OPPhMe_2$: (a) complex film prepared as described in the text; (b) sample from (a) following exposure to 53 torr of $^{16}O_2$ for 5 h; (c) sample from (b) following evacuation at ca. 10^{-6} torr for 48 h; (d) sample from (c) following further exposure to 48 torr of $^{16}O_2$ for 1 h; (e) sample from (d) following further exposure to 48 torr of $^{16}O_2$ for 24 h at room temperature.

tionalize the data. For example, the dioxygen could break a MnBr bridge and bind to an octahedral Mn containing the two phosphine ligands.[18] Then the superoxide could decompose to a complex having two alkoxyphosphine moieties followed by isomerization to the final phosphine oxide complex.

The Triethylphosphine Complex of $MnBr_2$. The behavior of the $MnBr_2PEt_3$ complex upon interaction with dioxygen is quite different from that of the $MnBr_2PMe_3$ complex. For example, for the $MnBr_2PEt_3$ complex film we have been able to achieve several cycles of exposure to dioxygen followed by evacuation during which the color changes from dark blue to a very faint blue or white, indicating possible reversible interaction of the complex with the dioxygen. This process is much slower for the solid-state films than it is for solutions and is accompanied by continual decomposition to the $MnBr_2OPEt_3$ complex at ambient temperature. The infrared spectra corresponding to a series of such cycles are shown in Figure 3.

Figure 3a represents the infrared spectrum of a film of $MnBr_2PEt_3$ prepared in the manner discussed earlier. This spectrum is quite different from that of gas-phase PEt_3, indicating that reaction of $MnBr_2$ and the phosphine has occurred. Following exposure of the film to $^{16}O_2$, the spectrum shown in Figure 3b was recorded. One notes that the only significant spectral developments are a new band at 1130 cm^{-1} and a greatly accentuated band at 1030 cm^{-1}. Upon exposure of another $MnBr_2PEt_3$ film to $^{18}O_2$ (Figure 3b′), the 1130-cm^{-1} band shifts to 1095 cm^{-1}, and a weak new feature is noted at 615 cm^{-1}. The 1030-cm^{-1} band again is accentuated but does not shift to lower wavenumber. We believe that the 1130/1095-cm^{-1} band most probably again corresponds to an O–O stretching mode for a superoxide linkage. The 615-cm^{-1} band was very weak but may correspond to an Mn–O vibrational mode for the superoxide species. This band was not evident for the spectrum in Figure 3b, but it could lie under the spectral features near 650 cm^{-1}. The corresponding band for $MnBr_2PMe_3$ occurred at 570/545 cm^{-1}; it is not clear why the band should lie at significantly higher wavenumber for the PEt_3 complex.

The 1030-cm^{-1} band cycles in intensity upon dioxygenation/evacuation cycles (see Figure 3a,b,c,d). However, the band does not shift to lower wavenumber upon exposure to $^{18}O_2$ (see Figure 3b′). This indicates that the band must correspond to a ligand vibrational mode. The fact that the band cycles in intensity upon dioxygenation/evacuation is reasonable evidence for a reversible interaction of dioxygen with the $MnBr_2PEt_3$ complex film. However, it should be noted that the band at 1130 cm^{-1} actually grows in intensity upon evacuation (Figure 3c). Thus while the complex reversibly interacts with dioxygen, it must exhibit a competing irreversible decomposition step to the phosphine oxide complex, which fortuitously has a P–O vibrational mode near 1130 cm^{-1}. After the complex loses its color upon extensive contact

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[18] We thank a reviewer for this comment.

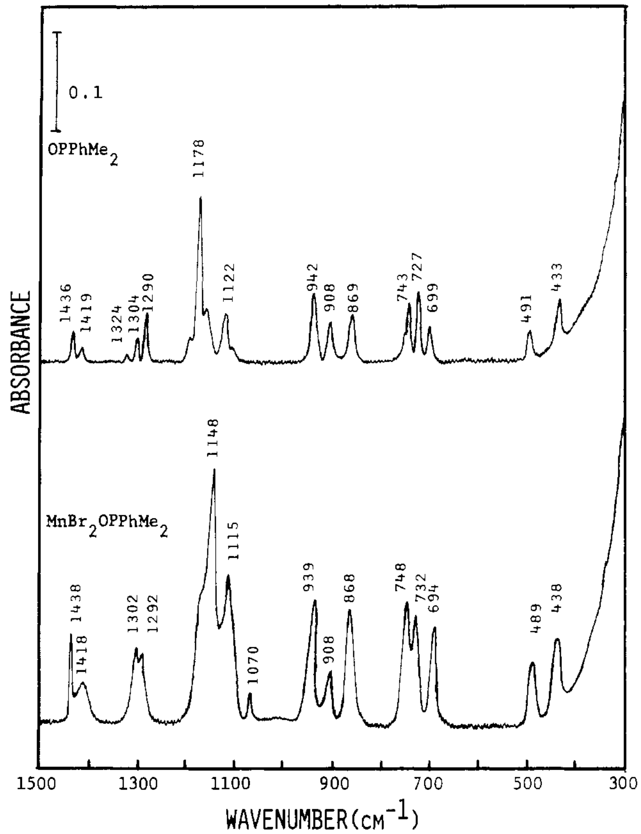

Figure 6. Infrared spectra of a solid-state film of OPPhMe$_2$ and a film of MnBr$_2$ exposed to sublimed OPPhMe$_2$.

with dioxygen, a large infrared band with its maximum at 1110 cm^{-1} (Figure 3e) is observed.

In summary, the MnBr$_2$PEt$_3$ complex seems to interact reversibly with dioxygen, whereas MnBr$_2$PMe$_3$ does not appreciably. However, MnBr$_2$PEt$_3$ also decomposes much more rapidly in dioxygen than does MnBr$_2$PMe$_3$ at ambient temperature. Whether the behavior of the MnBr$_2$PEt$_3$ complex in the presence of dioxygen can be explained by the reaction scheme in Figure 2 is not clear from this study. The band noted for a MnBr$_2$POMeMe$_2$ complex at 1060 cm^{-1}, which should shift when $^{18}O_2$ is employed, is not evident in any of the spectra shown in Figure 3. Of course, it could lie under the extensive band system at 1080–1000 cm^{-1}, such that its behavior could not be monitored.

The Phenyldimethylphosphine Complex of MnBr$_2$. The behavior of the MnBr$_2$PPhMe$_2$ complex in the presence of dioxygen is quite different from that of the two trialkyl complexes. We have observed several cycles of dioxygenation/evacuation by observation of color changes of the film; however, there are no infrared bands that cycle in intensity for this complex.

Figure 4 shows the infrared spectra of PPhMe$_2$ and an MnBr$_2$ film exposed to PPhMe$_2$. It is evident that significant changes in band intensities and wavenumbers have occurred, supporting our contention that an MnBr$_2$PPhMe$_2$ film has been produced.

Figure 5 illustrates the behavior of the MnBr$_2$PPhMe$_2$ complex upon exposure to $^{16}O_2$ and subsequent evacuation as evidenced by sequential infrared spectra. In Figure 5a a weak band occurs at 1109 cm^{-1}, which can probably be attributed to the P–C stretching vibrational mode for the phosphorus–phenyl linkage. The intensity of this band is accentuated upon exposure to dioxygen (Figure 5b). New bands also appear at 1148 and 435 cm^{-1} following exposure to dioxygen (Figure 5b), but these bands continue to develop even following evacuation (Figure 5c) and remain intense after the complex has lost its activity (Figure 5e). There is little doubt that these two bands may be assigned to the MnBr$_2$OPPhMe$_2$ decomposition product because Figure 5e is almost identical with the infrared spectrum of an authentic MnBr$_2$OPPhMe$_2$ film prepared by exposing MnBr$_2$ to OPPhMe$_2$ (Figure 6). Any band due to the dioxygen adduct MnBr$_2$PPhMe$_2$·O$_2$ (Figure 5b) must be masked by the intense phosphine oxide complex band at 1148 cm^{-1}. Furthermore, there was no new band detected in the 500–650-cm^{-1} region for the oxygenated complex, although a broad, weak band could easily be masked by the ligand band near 700 cm^{-1}, which has a broad low-energy shoulder (Figure 5). The fact that the band at 1148 cm^{-1} continues to grow during evacuation is evidence that under these reaction conditions a dioxygen adduct is rapidly decomposing to the MnBr$_2$OPPhMe$_2$ decomposition product.

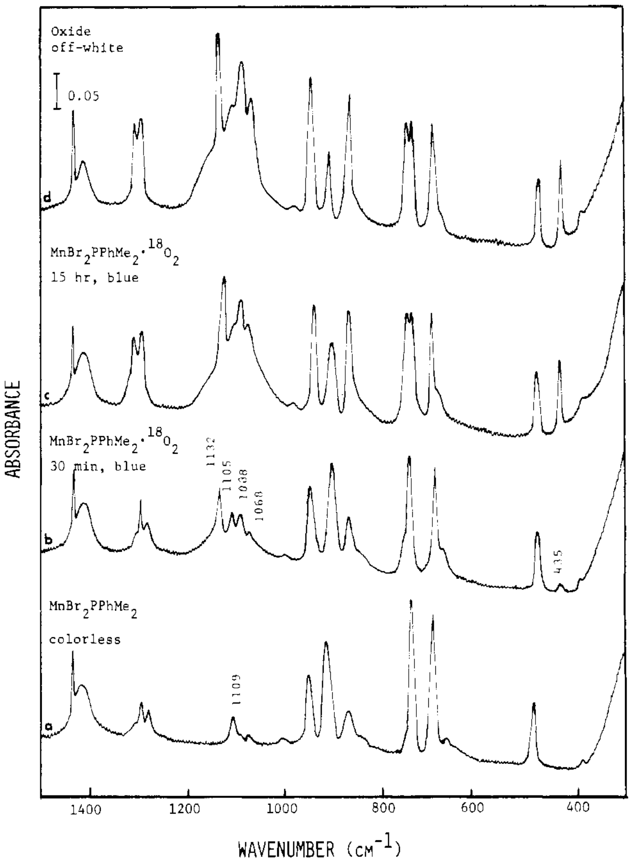

Figure 7. Infrared spectra of MnBr$_2$PPhMe$_2$, MnBr$_2$PPhMe$_2$·$^{18}O_2$, and MnBr$_2$^{18}OPPhMe$_2$: (a) complex film prepared as described in the text; (b) sample from (a) following exposure to 180 torr of $^{18}O_2$ for 30 min; (c) sample from (b) following further exposure to 180 torr of $^{18}O_2$ for 15 h; (d) sample from (c) following heating at 308 K in 180 torr of $^{18}O_2$ for an additional 72 h (subsequent evacuation caused no spectral or color changes).

Figure 7 shows the infrared spectra of an MnBr$_2$PPhMe$_2$ film exposed to $^{18}O_2$. Upon brief exposure the 1109-cm^{-1} ligand band shifts slightly to 1105 cm^{-1}, and two new bands are formed at 1132 and 1088 cm^{-1}. However, all of these bands remain for the final MnBr$_2$^{18}OPPhMe$_2$ decomposition product. Thus we must conclude that decomposition is rapid for MnBr$_2$PPhMe$_2$ in the presence of dioxygen. The only evidence for reversibility is the fact that the color disappears upon evacuation (Figure 5c) and reappears upon further exposure to dioxygen (Figure 5d). Of course, this observation could also be explained by incomplete reaction of MnBr$_2$PPhMe$_2$ (Figure 5b) with dioxygen before evacuation was initiated, such that some complex remained for reaction upon further exposure (Figure 5d). Thus although phenyldialkylphosphine complexes of MnBr$_2$ have been postulated to interact rapidly and reversibly with dioxygen in solution,[4] in a solid-state film the $MnBr_2PPhMe_2$ complex decomposes rapidly in competition with evacuation of the complexed dioxygen. Whether the reaction scheme proposed in Figure 2 is valid for this complex could not be determined in this work.

Conclusions

The interaction of dioxygen with tertiary phosphine complexes of $MnBr_2$ for solid-state films is markedly dependent upon the nature of the tertiary phosphine ligand employed. The $MnBr_2PMe_3$ complex is quite stable toward decomposition to $MnBr_2OPMe_3$ upon exposure to dioxygen, but it also shows little tendency toward reversibility during dioxygenation/evacuation cycles. In fact the blue color cannot be removed by prolonged evacuation, and it only disappears following decomposition. On the other hand, cycles of color/colorless can be obtained for $MnBr_2PEt_3$ and $MnBr_2PPhMe_2$ upon dioxygenation/evacuation, but these complexes decompose (especially $MnBr_2PPhMe_2$) competitively to the phosphine oxide complexes. The $MnBr_2PEt_3$ complex film was the only one in this study that exhibited an infrared band that clearly cycles in intensity upon dioxygenation/evacuation cycles. Finally, it should be noted that recent work here has demonstrated that the chloride analogues of the three complex films discussed in this work behave similarly to the bromide complex films.[19]

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Registry No. $MnBr_2PMe_3$, 85883-29-0; $MnBr_2PEt_3$, 82758-64-3; $MnBr_2PPhMe_2$, 71957-10-3; $MnBr_2PMe_3{\cdot}O_2$, 85893-33-0; $MnBr_2PMe_2OMe$, 92816-97-2; $MnBr_2OPMe_3$, 85883-30-3; $MnBr_2OPMe_2OMe$, 92816-98-3; $MnBr_2PEt_3{\cdot}O_2$, 92816-99-4; $MnBr_2OPEt_3$, 92817-00-0; $MnBr_2PPhMe_2{\cdot}{}^{16}O_2$, 72910-33-9; $MnBr_2{}^{16}OPPhMe_2$, 92817-01-1.

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[19] Newberry, V. F.; Hill, W. E.; Worley, S. D., unpublished data.

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Ring-Size Effects on the Formation of Dicopper(II) and Dicopper(III) Complexes with Bimacrocycles Containing 13- and 14-Membered Tetraaza Subunits

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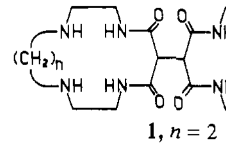
The double-ring macrocycle **1**, having 13-membered subunits, incorporates two Cu^{II} ions in aqueous solution according to three pH-controlled steps, which involve progressive deprotonation of the coordinated amido groups of the ligand. The fully deprotonated neutral dicopper(II) complex undergoes a reversible oxidation process to the dicopper(III) species according to two one-electron redox changes separated by 100 mV. This behavior is compared with that of the corresponding bimacrocyclic ligand having 14-membered subunits **2** as well as with the single-ring reference systems **3** and **4**. The 14-membered subunit forms the more stable complexes with Cu^{II} ion, whereas the 13-membered cavity favors the access to the trivalent state, with both single- and double-ring systems.

Introduction

Bimacrocycles are molecules in which two potentially chelating macrocyclic subunits are linked together. Each ring may coordinate a metal ion, and the two metal centers may display independent or mutually dependent behavior depending upon the length of the bridge joining the two subunits. The most favorable coordination of transition cations is that one containing four nitrogen atoms in the donor set, and some double-ring molecules with tetraaza subunits have been developed in the past years. All the reported bimacrocycles originated from metal template syntheses or from reactions involving preformed monocyclic metal complexes.[1-3] As a consequence, macrocyclic subunits of fixed ring size were obtained, preferably the 14-membered ones.

We have recently developed a new synthetic strategy for the preparation of bimacrocycles containing tetraaza subunits, simply based on the condensation of a tetraester (tetraethyl 1,1,2,2-ethanetetracarboxylate) with a linear tetraamine in a 1:2 molar ratio.[4,5] In this way, the double-ring macrocycle, in which two dioxo tetraamine subunits are linked by a covalent bond between two atoms of the carbon backbones, is obtained as a free, uncomplexed molecule. Moreover, the method is particularly flexible, since when the length of the tetraamine fragment used in the condensation is modulated, bimacrocycles containing subunits of varying ring size can be obtained. In a previous report the coordinating behavior of a bimacrocycle with 14-membered rings, ([14-14]bisdioxocyclam (**2**)), has been described.[5] We report here the chelating tendencies of the 13-membered analogue, ([13-13]bisdioxocyclam (**1**)).



1, $n = 2$
2, $n = 3$

Dioxo tetraamine macrocycles and their metal complexes present some interesting properties. (*i*) The dioxo tetraamine ring can incorporate a divalent 3d cation (e.g., Cu^{II}) with a simultaneous extrusion of two hydrogen ions from the amido groups;[6] therefore, complexation is pH dependent and can be monitored through potentiometric titration. (ii) When en-

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