Inorganica Chimica Acta, 30 (1978) L291–L293

Reversible μ-Peroxo Complexes of Manganese(II)

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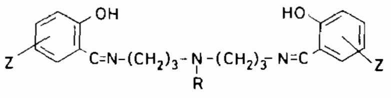
Received June 12, 1978

Initial oxygenation studies involving manganese(II) chelates suggest that a greater variety of metal–oxygen linkages will be possible than has been observed with comparable more common cobalt(II) complexes [1]. While μ-oxo [2], μ-peroxo [3], polycatena-oxo [3], di-μ-oxo [4] and di-μ-hydroxo [5] structures have been postulated to arise from interaction with oxygen only two studies (μ-oxo and di-μ-hydroxo) are supported by X-ray structural analysis. Evidence has recently been presented [6] that suggests that the latter may be better formulated as a di-μ-oxo species. The proliferation of manganese-oxygen linkages has continued as evidenced by ESR low temperature solution studies [7] of oxygenated [Mn(TPP)(Py)] where TPP = tetraphenylporphyrinato dianion. The formation of $(TPP)Mn^{IV}–O_2^{2-}$ is suggested; however, no products were isolated.

Evidence has recently been presented with shows that manganese(II) complexes incorporating pentadentate ligands derived from substituted salicylaldehydes and triamines (*i.e.* Mn(ZSALRDPT), Structure I), readily react with oxygen. Initially manganese(III) species are produced which in turn are further susceptible to ligand oxidation. Employment of a strongly electron withdrawing group on the salicylaldehyde portion (NO_2) retards the ligand oxidation enough in order that a characterizable high spin manganese(III) material is obtained, [Mn(5-NO_2SALRDPT)(OH)]. In that report it was postulated that hydrolysis of a μ-peroxo material resulted in the formation of the hydroxo complex. We wish to describe in a preliminary fashion the oxygenation reaction under highly anhydrous conditions and the products obtained therefrom.



H_2ZSALRDPT

Structure I

The extent and rate of dry O_2 uptake for Mn(ZSALDPT) (R = H) partially dissolved in dry toluene parallels the results obtained using "wet" O_2 and "wet" toluene. Again only the 5-NO_2 derivative gives an isolable product, but an examination of this material suggests a compound different from an hydroxy species. Complete elemental analyses on this material coupled with O_2 uptake measurements (n_{O_2}/n_{Mn} = 0.5) suggest an emprirical formula of Mn(5-NO_2SALDPT)(O). An identical compound except for a $CHCl_3$ solvate is obtained by oxygenation of a $CHCl_3$ solution of Mn(5-NO_2SALDPT). The characteristic 620 cm^{-1} band attributable to a Mn–O stretch appears in the infrared spectrum of both compounds, however, the bands at 3600 cm^{-1} and 1200 cm^{-1} observed in the hydroxo species are absent. Extension of this toluene and chloroform study to the anhydrous 3-NO_2 derivative gives two analogous materials regardless of whether the O_2 and solvents are wet or dry.

While the 3-NO_2 and 5-NO_2 derivatives display similar O_2 reactivity and stoichiometry subtle differences appear in the physico-chemical properties of their oxygenation products. For example, the 5-NO_2 product from toluene or chloroform exhibits a magnetic moment of 4.9 B.M.; whereas, the 3-NO_2 derivative regardless of the solvent has μ_{eff} = 2.9 B.M. A cursory interpretation of these results suggests a high and low spin manganese(III) complex for the 5-NO_2 and 3-NO_2 cases respectively. Alternatively, the lower magnetic moment for 3-NO_2 may arise from spin–spin coupling between manganese centers; however, magnetic measurements down to 4 °K in both the 5-NO_2 and 3-NO_2 cases show no dependence of μ_{eff} on temperature.

Thermal gravimetric analyses (TFA) on the oxygenation products reveal significant weight losses on heating *in vacuo*. Here again the two materials behave differently. Weight loss equivalent to 32 a.m.u./formula unit in the 5-NO_2 (toluene and $CHCl_3$) case occurs *ca.* 150 °C but at 100 °C *in vacuo* the 3-NO_2 (toluene and $CHCl_3$) experiences comparable weight loss. Magnetic susceptibility measurement on the material remaining after the TGA experiment was performed yielded μ_{eff} = 5.5 B.M. (5-NO_2), 5.6 B.M. (3-NO_2) which suggests that the loss in weight is accompanied by regeneration of the manganese(II) precursor. Low temperature esr spectra of the deoxygenated materials dissolved in toluene/CH_2Cl_2 gave absorptions at g = 2.007, and g = 4.217, again consistent with a manganese(II) species. The signal around g = 2 was split into a six-line pattern with a coupling constant of 91 gauss.

In an effort to demonstrate that the material being lost on thermal analysis is molecular oxygen, $[Mn(5\text{-}NO_2SALDPT)]_2O_2\cdot CHCl_3$ was examined employing thermal gravimetry combined with chemical ionization (reagent gas = Ar) mass spectro-

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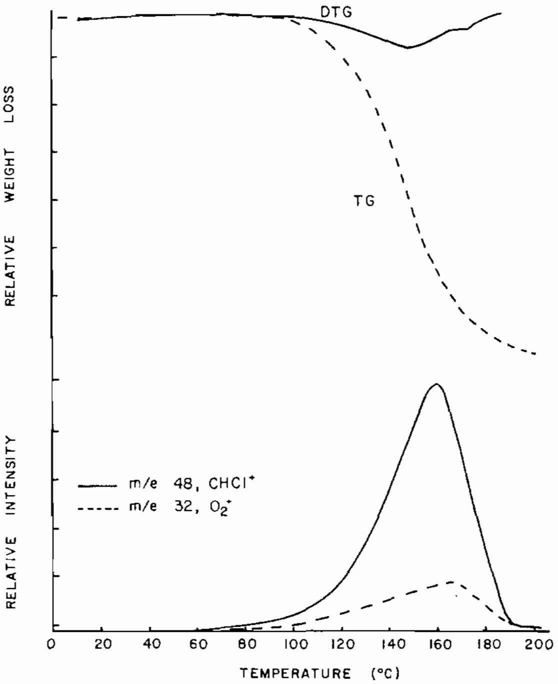

Figure 1. TG/DTG curves and MS profile of [Mn(5-NO_2-SALDPT)]$_2O_2$·$CHCl_3$.

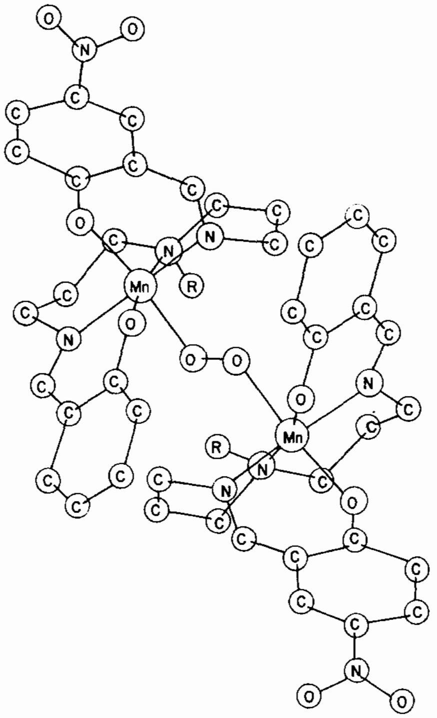

Figure 2. Suggested structure for [Mn(5-NO_2SALDPT)]$_2O_2$.

metry (TG–CIMS). This technique has recently been described [9] as an ideal method for the detection of volatiles that may be produced in chemical reactions or released as part of a thermal decomposition process. Mass to charge ratios of 32, 33, 48, 118 and 120 a.m.u. were monitored during the experiment. Around 150 °C signals for masses 32 a.m.u. and 48 a.m.u. were observed whereas, response at the remaining three masses was insignificant. These observations correlated quite well with simultaneous thermal gravimetry measurements (Figure 1). The m/e at 32 a.m.u. and 48 a.m.u. are believed to arise from O_2 and the $HCCl^+$ ion of $CHCl_3$ respectively. The concurrent loss of O_2 and $CHCl_3$ at the same temperature suggests that the solvent adduct is critical toward stabilizing the Mn–O_2 linkage. As a check of the system a related complex [10] [Mn(SALDPT)NO] · $CHCl_3$ was examined. A signal for mass = 30 a.m.u. appeared at ~140 °C assignable to NO while no signal at mass = 32 a.m.u. was found as expected.

The reactivity of [Mn(5-NO_2SALDPT)(OH)] as well as its solubility properties differed from [Mn(5-NO_2SALDPT)]$_2O_2$. The μ-peroxo product is insoluble in THF; whereas, the hydroxy material is very soluble in THF. Suspension of [Mn(5-NO_2-SALDPT)]$_2O_2$ in THF followed by addition of H_2O resulted in evolution of a gas presumed to be O_2. Testing this solution for H_2O_2 gave a negative test. If this reaction is carried out in an anerobic environment, the final yellow colored solution yields an ESR signal attributable to a high spin Mn(II) species. A yellow precipitate volunteers after allowing the solution to stand overnight (μ_{eff} = 5.60 B.M.). Suspending this yellow material in toluene and exposing to the air causes loss of the yellow color and accompanying esr signal. Treatment of the 3-NO_2 derivatives suspended in THF with water, dilute acid or base did not evolve O_2. Decomposition of the complex with the formation of a black tarry substance was observed.

The nature of these reversibly formed oxygenation materials is uncertain. Efforts to grow crystals for x-ray structural analysis have been unsuccessful because of their insolubility in a suitable solvent. It is not, however, unreasonable to expect these Mn(II) complexes to undergo oxygenation in a manner similar to the analogous isomorphous [11] Co(II) complexes. For this reason coupled with the available analytical data, we propose that these new oxygenation products are the first well documented μ-peroxo manganese(III) compounds. A suggested structure for these materials is shown in Figure 2 which is similar to the structure found for [Co-(SALDPT)]$_2O_2$·$C_6H_5CH_3$ [12].

With the isolation of μ-peroxo materials and regeneration of precursor on reaction with H_2O considerable insight is available regarding the oxygenation of these Mn(II) complexes. The following scheme may be envisioned (1, 2) wherein Mn(II) is rapidly oxidized toMn(III). Figure 3 illustrates the emergence of the d–d band in the visible spectrum typical of Mn(III) accompanying oxygenation. The production

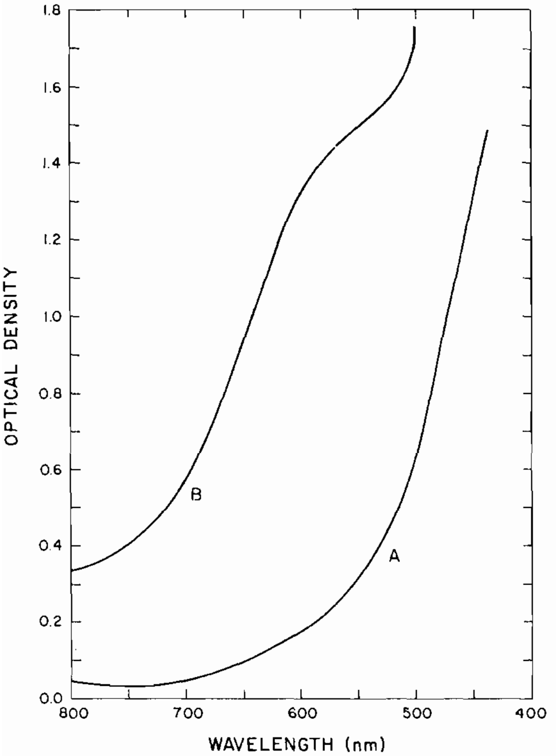

Figure 3. Visible spectrum of $Mn(5\text{-}NO_2SALDPT)$ (0.001*M*) in $CHCl_3$ before (A) and after (B) exposure to O_2 for 40 minutes.

$$Mn^{II}L + O_2 \rightleftharpoons LMn^{III}\text{–}O_2 \qquad (1)$$

$$LMn^{III}\text{–}O_2^- + LMn^{II} \rightleftharpoons LMn^{III}\text{–}O_2^{2-}\text{–}Mn^{III}L \qquad (2)$$

of the Mn^{III}–OH apparently does not proceed via the μ-peroxo species as originally proposed [8] (3). Regeneration of an hydrated Mn(III) complex followed successively by outer sphere oxidation and hydrolysis (4–5) is more consitent with the data at this time.

$$LMn^{III}\text{–}O_2^{2-}Mn^{III}L + H_2O \longrightarrow LMn^{III}\text{–}OH + H_2O_2 \qquad (3)$$

$$LMn^{II}\text{–}(OH_2) \longrightarrow LMn^{III}\text{–}(OH_2) \qquad (4)$$

$$LMn^{III}\text{–}(OH_2) \longrightarrow LMn^{III}\text{–}OH + H^+ \qquad (5)$$

Further support for the μ-peroxo formulation is provided by investigation of similar complexes wherein the secondary nitrogen is substituted. Dimerization should be inhibited by alkyl groups on the central nitrogen (Figure 2). Under anhydrous conditions in toluene or $CHCl_3$ [$Mn(5\text{-}NO_2SALMeDPT)(OH)$] is produced in poor yield. [$Mn(3\text{-}NO_2SALMeDPT)]_2O_2$ is, however, the major material on oxygenation and possesses the same magnetic and deoxygenation properties as the DPT analog. It is obvious that the $3\text{-}NO_2$ derivatives have a much different electronic effect on manganese than the $5\text{-}NO_2$ derivatives and presumably this electronic effect is able to overcome any steric problems presented by the methyl group in the formation of a μ-peroxo species.

Acknowledgement

The financial support provided by NIH Research Grant GM 21844-01 from the National Institute of General Medical Sciences is appreciated. We wish to thank E. Baumgartner and E. Nachbaur for kindly performing the TG-CIMS measurements.

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