Air Oxidation of a Manganese(III) Thioether Chelate affords the First Manganese(III) Dihydrosalen Complex with a Pendant Sulfoxide Ligand

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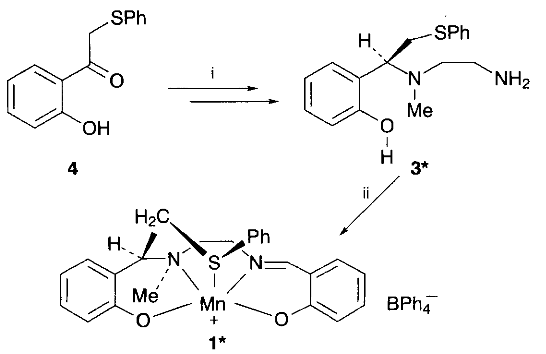
The aerobic oxidation of the manganese(III) dihydrosalen-thioether chelate *rac*-**1** affords the novel manganese(III) sulfoxide complex *rac*-**2**; X-ray structural analysis of the latter reveals that only one of the two possible diastereomeric oxidation products is present in the crystal.

The selective oxygenation of organic substrates with molecular oxygen is a challenging goal for both laboratory and industrial applications.[1] In nature, dioxygen is the terminal oxidant for oxygen metabolizing enzymes, like monooxygenases. With respect to preparative applications, these systems and most of their synthetic analogues suffer from the disadvantage that reducing equivalents are required. In the course of oxygen activation, one atom of the O_2 molecule is reduced to water, while the other one is used for substrate oxidation.[2] As a rare exception, ruthenium catalysts have successfully been employed for the epoxidation of alkenes and the oxidation of sulfides to sulfoxides with molecular oxygen in the absence of co-reductants.[3] Herein we report the air oxidation of the manganese(III) thioether complex *rac*-**1** to the sulfoxide complex *rac*-**2**, also *without* added reducing equivalents.

The diamine *rac*-**3** was used as a precursor in the synthesis of the complex *rac*-**1** (Scheme 1). It was prepared in four steps starting from ketone **4**.[4] The manganese(III) thioether complex was obtained by first preparing the Schiff's base from salicylaldehyde and the diamine *rac*-**3** in methanol. The resulting yellow solution turned dark brown immediately after addition of manganese(II) chloride tetrahydrate in the presence of air. The manganese(III) thioether complex *rac*-**1** was finally precipitated (as the monohydrate) from this solution as a microcrystalline brown powder by addition of sodium tetraphenylborate at −21 °C.†

The manganese(III) chelate *rac*-**1** proved succeptible to air oxidation in solution: whereas its rapid crystallization from ethyl acetate–*n*-hexane afforded a brown powder of unchanged composition, prolonged exposure to oxygen resulted in the formation of a new material which was monooxygenated according to its FD-MS data.‡ The slow evaporation of an aerated chloroform solution finally afforded dark brown crystals, suitable for X-ray structural analysis. The result, which identified the oxygenation product as the sulfoxide complex *rac*-**2**, is shown in Fig. 1.§ The sulfoxide complex *rac*-**2** crystallizes as a water bridged [O(1w), O(1wa), Fig. 1] centrosymmetric dimer in which the manganese ions are pseudo-octahedrally coordinated. The O- and N-atoms of the dihydrosalen moiety of the ligand occupy equatorial positions, whereas the sulfoxide O-atom is located at a fifth, axial coordination site. Finally, the pseudo-octahedral coordination geometry around the manganese ion is completed by an axial water molecule [O(1w), O(1wa), Fig. 1].

For the metal catalysed conversion of thioethers to sulfoxides by molecular oxygen, high pressures of oxygen and elevated temperatures,[5] or the addition of reducing agents[6] are usually required. Our results represent the first example of a manganese(III)-mediated air oxidation of a thioether at atmospheric pressure and at ambient temperature, without added reducing equivalents. At the present stage, a mechanistic discussion of the unprecedented conversion of *rac*-**1** to *rac*-**2** must still be rather speculative. Nevertheless, since manganese(III) complexes of the salen or porphyrin type are usually d^4 high-spin in nature,[7] reversible addition of an O_2 molecule to the sixth



Scheme 1 *Reagents and conditions*: i, 4 steps, 40% overall yield; ii, salicylaldehyde, $MnCl_2{\cdot}4H_2O$, O_2, $NaBPh_4$, 39% yield. Asterisk denotes racemic mixture.

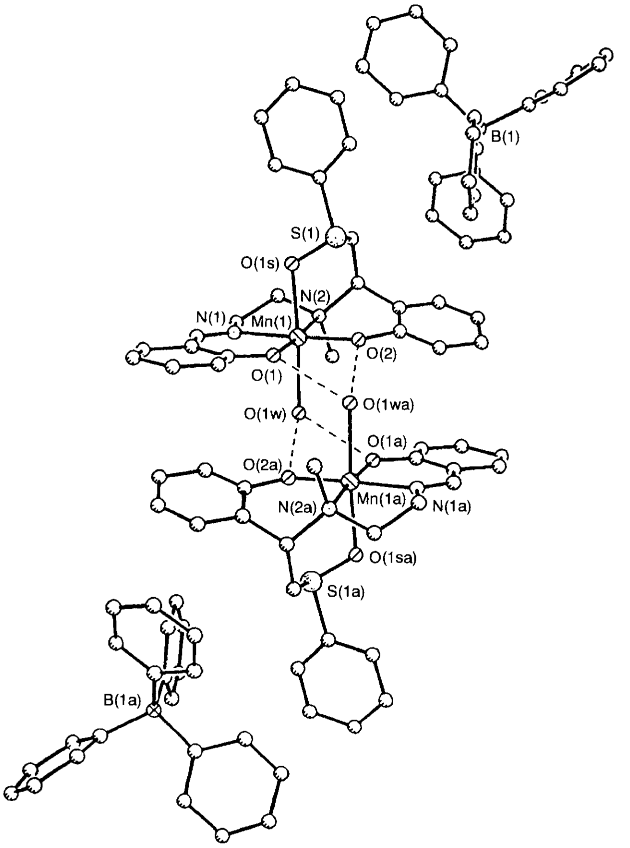
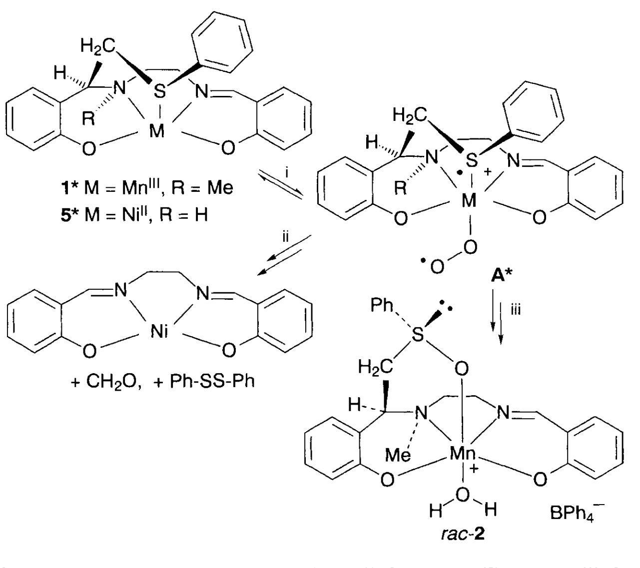


Fig. 1 X-Ray structural analysis of the manganese(III) sulfoxide complex *rac*-**2**. View of the water bridged centrosymmetric dimer. Selected interatomic distances (Å) and angles (°): Mn(1)–O(1) 1.884(7); Mn(1)–O(2) 1.851(7); Mn(1)–N(1) 2.012(11); Mn(1)–N(2) 2.085(9); Mn(1)–O(1s) 2.187(9); Mn(1)–O(1w) 2.315(8); S(1)–O(1s) 1.490(8); Mn(1)–O(1s)–S(1) 115.5(5); O(1w)–Mn(1)–O(1s) 176.1(3). The averaged deviation from planarity of the atoms Mn(1), O(1), O(2), N(1), N(2) is 0.012 Å.

coordination site of *rac*-**1** (occupied by a water molecule in the crystal structure of *rac*-**2**) appears quite likely. Furthermore, the oxidation of a pendant thioether ligand by dioxygen coordinated to the opposite axial site of the metal ion has precedent in the air-induced degradation of the nickel(II) dihydrosalen complex *rac*-**5**[8] (Scheme 2). In the case of *rac*-**5**, air oxidation results in the formation of nickel(II) salen, formaldehyde and diphenyl disulfide. The latter two products result from the degradation of the pendant phenylthiomethyl group. Mechanistic investigations[8] suggested that the oxidation of the complex *rac*-**5** is initiated by reversible addition of O_2 to the vacant axial coordination site (**A**, Scheme 2). The coordinated O_2 molecule is formally reduced to superoxide. The extra electron stems from the coordinated thioether, which is thus oxidized to the radical cation. The electron transfer from the thioether to the bound O_2 molecule is mediated by the metal ion. In *rac*-**5**, the fragmentation of the ligand is finally induced by homolytic H-abstraction from the coordinating NH group by the bound superoxide ligand[8] (**A**, Scheme 2). Clearly, the *N*-methylated ligand of *rac*-**1** is not susceptible to this type of attack by bound superoxide.[9] Thus, binding of dioxygen to *rac*-**1** may as well be envisaged to cause a metal-mediated oxidation of the pendant thioether, but not a fragmentation of the ligand. This is exactly what was observed. Instead, attack of water at the thioether radical cation[10] and concomitant reduction of the bound superoxide to hydrogen peroxide may be regarded as the final steps in the conversion of *rac*-**1** to the sulfoxide complex *rac*-**2**.

The crystals of *rac*-**2** used for the X-ray structural analysis consisted only of the diastereomer shown in Fig. 1. Clearly, oxidation of *rac*-**1** may as well be expected to yield a sulfoxide with opposite relative configuration at the sulfur atom. At present, we cannot distinguish a diastereoselective oxygenation at the thioether sulfur atom from diastereoselective crystallization. Unfortunately, the NMR spectroscopic investigation of the product composition in solution is severely hampered by the paramagnetism of the manganese(III) complexes *rac*-**1**,**2**. Nevertheless, our results suggest the general possibility of stereoselective sulfoxide formation with air as oxidant in the presence of chelating manganese(III) ions.



Scheme 2 *Reagents and conditions*: i, O_2; ii, for M = Ni^{II}, R = H; iii, for M = Mn^{III}, R = Me. Asterisk denotes racemic mixture.

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Footnotes

† The elemental analysis (C,H,N) of *rac*-**1** was satisfactory within 0.3%. FD-MS showed a signal at *m*/*z* 459, assigned to the cation $C_{24}H_{24}MnN_2O_2S$.

‡ A solution of 100 mg (125 μmol) of *rac*-**1** (*m*/*z* 459) in 10 ml of ethyl acetate was stirred under an atmosphere of oxygen (1 bar). After 48 h, addition of *n*-hexane resulted in the precipitation of 90 mg (87%) of the oxygenation product as a microcrystalline brown powder. Analysis by FD-MS showed one signal at *m*/*z* 475 ($C_{24}H_{24}MnN_2O_3S$, product *rac*-**2**).

§ *Crystal data* for *rac*-**2**: $C_{48}H_{46}BMnN_2O_4S$, M = 812.68, triclinic, space group $P\bar{1}$, a = 13.538(4), b = 13.779(3), c = 14.331(3) Å, α = 103.17(2), β = 104.11(2), γ = 107.65(2)°, V = 2335.2(10) Å^3, Z = 2, D_c = 1.156 g cm^{-3}, intensities were recorded for 6059 unique reflections (θ range 6.49–60.05°) on an Enraf Nonius CAD4 diffractometer using Cu-Kα-radiation, 6059 symmetry-independent reflections; an empirical absorption correction was made by using the program DIFABS,[11] 6057 reflections were used for the structure solution (SHELXTL PLUS program system); wR (based on F^2) = 0.410; data/parameter ratio = 11.8 : 1, maximum residual electron density 0.84 e Å^{-3}. Further details of the crystal structure investigation of *rac*-**2** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-58450, the names of the authors and the journal citation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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