Detection of EPR spectra in $S = 2$ states of Mn^{III}(salen) complexes

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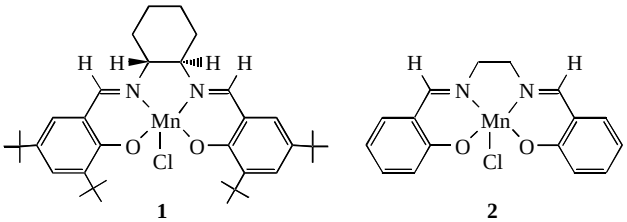
The EPR signals of Mn^{III}(salen) complexes (*R*,*R*)-(–)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride **1 and *N*,*N*′-bis(salicylidene)ethylenediaminomanganese(III) chloride **2** were detected and used for the characterisation of intermediates in catalytic epoxidation.**

A recent major achievement in catalytic enantioselective oxidation is the epoxidation of prochiral unfunctionalised olefins catalysed by Mn(salen) complexes.[1–4] Two practicable catalytic systems for the enantioselective epoxidation of unfunctionalised olefins were developed. One of them involves a two-phase system with commercial aqueous buffered bleach phase and an organic phase that is a solution of a substrate and a catalyst in a suitable solvent.[1] The other system is a solution of *m*-chloroperbenzoic acid (*m*-CPBA), *N*-methylmorpholine *N*-oxide (NMO) and a catalyst in dichloromethane at a low temperature (–78 °C).[5,6] The latter system is effective in the enantioselective epoxidation of styrene.[5]

To elucidate the mechanism of Mn^{III}(salen)-catalysed oxidation, it is important to monitor transformations of the catalyst in the course of the catalytic reaction. In this work, we report the first EPR data on Mn^{III}(salen) complexes (*R*,*R*)-(–)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride **1** and *N*,*N*′-bis(salicylidene)ethylenediaminomanganese(III) chloride **2** in various solvent systems. The preliminary data on the interaction of complex **1** with iodosylbenzene (PhIO) and *m*-CPBA are also presented.



1 **2**

EPR spectroscopy has rarely been applied to study the electronic structure of trivalent manganese complexes with an even number of unpaired electrons. This is a result of large zero-field splittings or fast spin relaxation processes. Although a few of EPR studies of trivalent manganese impurity ions and complexes have been reported, these have relied largely on indirect detection methods or very high observation frequencies.[7–10] There is the only report where weak EPR transition at $g \approx 8$ was observed for manganese(III) acetylacetonate at 12 K by conventional X-band EPR spectroscopy.[11] Dexheimer *et al.* interpreted the Mn^{3+} spectrum using the following spin Hamiltonian:

$$H = \beta(g_z H_z S_z + g_y H_y S_y + g_z H_z S_z) + D(S_z^2 - 2) + E(S_z^2 - S_y^2) \qquad (1)$$

The zero-field interaction splits the levels of an $S = 2$ spin system into two doublets, one of them is a linear combination of the $m_s = |\pm 2\rangle$ states, and the other, of the $m_s = |\pm 1\rangle$ states, and a singlet corresponding to the $m_s = |0\rangle$ state. The forbidden EPR transitions may be observed between the levels of the $|\pm 2\rangle$ non-Kramers doublet.

The X-band EPR spectrum of a frozen 0.1 M solution of complex **1** in CH_2Cl_2 at 77 K is shown in Figure 1(*a*).† The field position and shape of the observed weak signal at $g = 8.0 \pm 0.3$ are close to those for the signal observed for manganese(III) acetylacetonate and attributed to forbidden transitions within $|\pm 2\rangle$ non-Kramers doublet.[11] The relatively sharp resonance at $g = 4.3$ is characteristic of rhombic Fe^{III} complexes and belongs to very small impurities (less than 1 mol%) of Fe^{III} species in complex **1**. The addition of $FeCl_3 \cdot 6H_2O$ to a solution of complex **1** gives rise to a sharp increase in the signal at $g = 4.3$. The Fe^{III} impurities were detected not only in our particular sample. The EPR spectrum of the optical isomer of

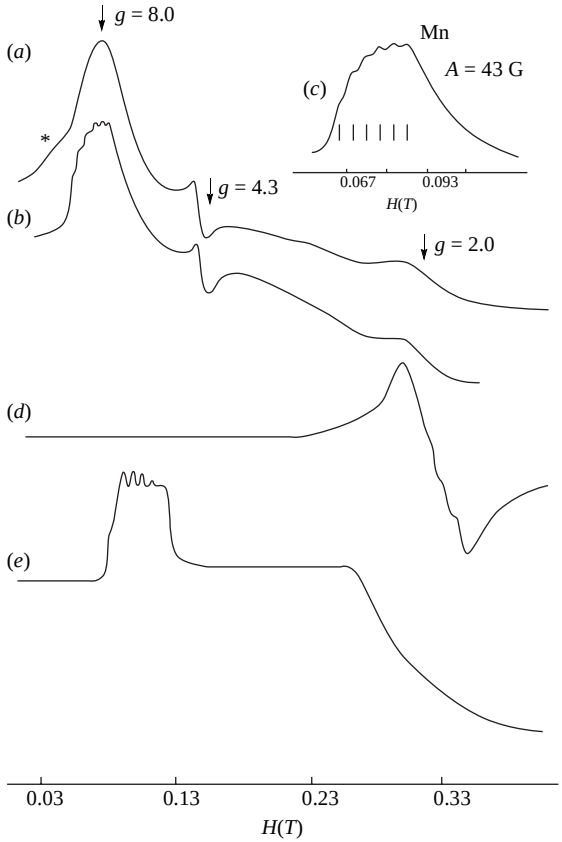


Figure 1 X-band EPR spectra (77 K) of 0.05 M solutions of complex **1** (*a*) in CH_2Cl_2 and (*b*)–(*c*) in CH_2Cl_2 containing *N*-methylmorpholine *N*-oxide ([NMO] = 1 M); (*d*) EPR spectrum (77 K) of 0.05 M solution of a Mn^{II}(salen) precursor of complex **2** in DMSO; (*e*) EPR spectrum (77 K) of Mn^{IV}(salen) complex recorded 1 min after the onset of reaction of complex **1** ([**1**] = 0.05 M) with one equivalent of *m*-chloroperbenzoic acid at 273 K [spectrometer frequency, 9.3 GHz; microwave power, 40 mW; modulation frequency, 100 kHz; modulation amplitude, 20 G; gain, 2.5×10^5 (*a*)–(*c*), 2.5×10^3 (*d*), 2.5×10^4 (*e*)].

† *General experimental details*. Complex **1** [(*R*,*R*)-(–)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride] and *N*-methylmorpholine *N*-oxide from Aldrich were used as received. Iodosylbenzene was prepared by hydrolysis of the corresponding diacetate (Aldrich) with aqueous sodium hydroxide and stored at 253 K. Complex **2** [*N*,*N*′-bis(salicylidene)ethylenediaminomanganese(III) chloride] and its Mn^{II} precursor were prepared as described in ref. 12. All other chemicals and solvents were of reagent grade, and they were used without further purification. EPR spectra were recorded in quartz tubes ($d = 5$ mm) at 77 K using a Bruker ER-200D X-band spectrometer.

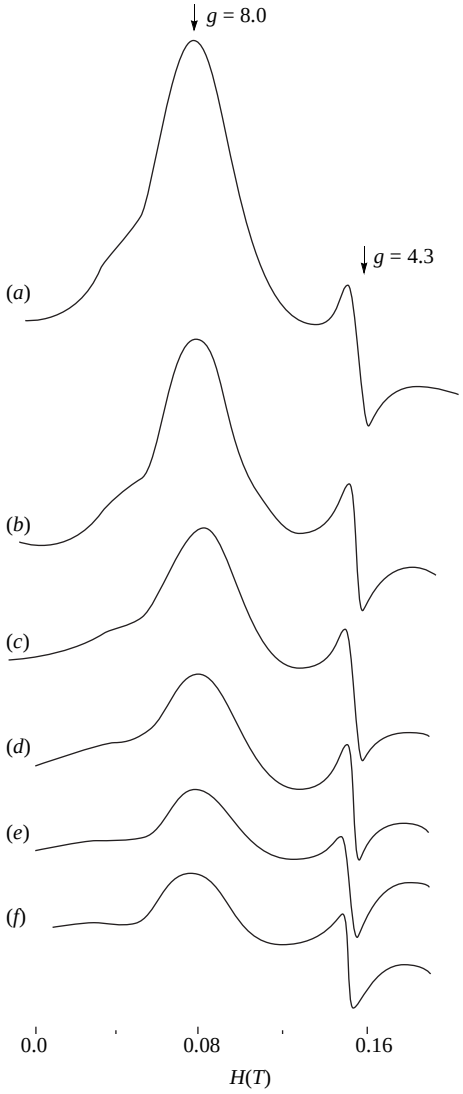


Figure 2 X-band EPR spectra (77 K) of 0.05 M solutions of complex **1** (*a*) in CH_2Cl_2 and (*b*)–(*f*) in CH_2Cl_2 containing various amounts of pyridine: (*b*) [Py] = 0.0125 M, (*c*) 0.025 M, (*d*) 0.0375 M, (*e*) 0.05 M, (*f*) 0.1 M. The spectrometer settings are given in Figure 1.

complex **1** (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride **1′** (Aldrich) also exhibited a resonance signal at $g = 4.3$ but its intensity was lower than that in complex **1** by a factor of two. The signals at $g = 8.0$ for complexes **1** and **1′** coincided. The nature of the additional low-field line marked in Figure 1(*a*) with an asterisk is still unclear.

Coordination of *N*-methylmorpholine *N*-oxide to complex **1** changes the shape of the EPR signal, and the six-line hyperfine structure from one manganese ion ($I = 5/2$) can be clearly seen [Figures 1(*b*)–(*c*)]. The hyperfine splitting (44±3 G) that appears at the $g = 8$ signal is rather close to that determined for Mn^{III} impurity ions in TiO_2 ($A_z = 53$ G)[10] and for manganese(III) acetylacetonate ($A_z = 55$ G).[11]

We have compared the EPR signals of 0.1 M solutions of complexes **1** and **2** in dimethylsulfoxide (DMSO) at 77 K. DMSO was used as a solvent owing to proper solubility of both complexes. The positions, shapes and intensities of the signals observed at $g = 8.0$ for complexes **1** and **2** coincided. This result supports the assignment of a resonance at $g = 8.0$ to complex **1** rather than to any manganese impurities. It is improbable that the concentrations of such impurities were equal in complexes **1** and **2**.

Low-symmetry $S = 5/2$ Mn^{II} species, which may be present as impurities in Mn^{III} compounds, can also give rise to downfield EPR signals. The two species can be clearly distinguished, however, because the $S = 5/2$ Mn^{II}(salen) system produces very intense resonance at $g = 2.0$ in addition to any other downfield signals. Figure 1(*d*) shows the EPR spectrum of a Mn^{II}(salen) precursor of complex **2** in DMSO, which was prepared according to the procedure described in ref. 12. This spectrum was recorded at an amplification lower than that in Figure 1(*a*) by two orders of magnitude. It is seen that Mn^{II}(salen) exhibits an intense signal at $g = 2.0$ with the partially resolved hyperfine splitting (87 G) from the manganese nucleus.

The Mn^{IV}(salen) complex obtained *via* a reaction of complex **1** with one equivalent of *m*-CPBA in CH_2Cl_2 at 273 K exhibits a resonance at $g = 5.7\pm0.3$, with the hfs splitting (73 G) from manganese nucleus typical of Mn^{IV} species with $D > h\nu$[13–16] [Figure 1(*e*)]. The amplification in Figure 1(*e*) is lower than that in Figure 1(*a*) by one order of magnitude, while concentrations of Mn^{III} and Mn^{IV} species are equal. Thus, the signal of Mn^{III}(salen) is much weaker than that of Mn^{IV}(salen) at equal manganese concentrations. This result agrees with the literature data. It was found for manganese impurity ions in TiO_2 that the resonances of Mn^{III} are about an order of magnitude weaker than those of the same quantity of corresponding Mn^{IV} species.[10] Based on the aforesaid, we can conclude that it is mononuclear Mn^{III}(salen) complex **1** that exhibits the EPR signal at $g = 8.0\pm0.3$. Dimers or higher aggregates of **1** can be ruled out. Based on the data for Mn^{III}/Mn^{IV} and Mn^{II}/Mn^{III} mixed-valence binuclear complexes, more than six line hyperfine splitting is expected for dimeric or oligonuclear species.[17,18]

The EPR signal of complex **1** was found to be very sensitive to the nature of axial ligands [compare Figures 1(*a*) and 1(*b*)]. Another illustration of this fact is presented in Figure 2. It can be seen, that the intensity and shape of the resonance at $g = 8.0$ dramatically changed with an increase in the concentration of

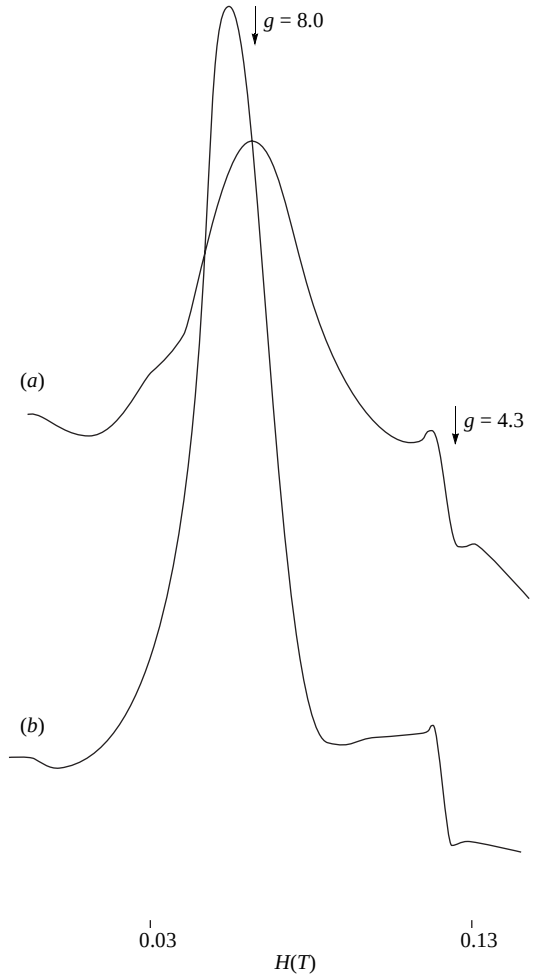


Figure 3 (*a*) X-band EPR spectrum (77 K) of a 0.05 M solution of complex **1** in CH_2Cl_2; (*b*) EPR spectrum of sample (*a*) 3 min after stirring with one equivalent of PhIO at 273 K.

pyridine in the solution of complex **1**. This change was stopped when the [Py]/[**1**] ratio reaches unity, in agreement with the coordination of one pyridine molecule per molecule of complex **1**. The reason for the decrease of the EPR signal of complex **1** *via* pyridine coordination is still unclear. It is known that axial ligands dramatically affect the *D* value in Mn^{III} porfirazine complexes.[11] Unfortunately, we have not found the relations between the *D* value and the probability of the $|-2\rangle \rightarrow |+2\rangle$ transition in the literature.

The interaction of complex **1** with one equivalent of *m*-CPBA at 183 K in CH_2Cl_2 gives rise to an immediate five-fold decrease in the intensity of the resonance at $g = 8.0$ similarly to that observed in Figure 2 *via* pyridine coordination. The valent state of manganese remains unchanged during this reaction, because a very weak signal of Mn^{IV} can be detected. Thus, the observed drop of the intensity of the EPR signal at $g = 8.0$ is caused by the conversion of complex **1** into another Mn^{III} complex, which is characterised by a lower intensity of the Mn^{III} resonance. This complex will be referred to as complex **3**. Complex **3** is extremely unstable. It exists only at 183–213 K and rapidly and quantitatively decomposes at higher temperatures to form metastable Mn^{IV} species, which were detected by EPR. By analogy with the well-known formation of acylperoxo complexes *via* the interaction of Mn^{III} porphyrins with *m*-CPBA at low temperatures,[19] it is reasonable to suggest that complex **3** is the acylperoxo complex Mn^{III}(salen)(OOCOAr). The reactivity of this complex toward alkenes will be further investigated.

An interesting behaviour was observed in the interaction of complex **1** with PhIO. Immediately after 3 min stirring of a 0.05 M solution of complex **1** with a suspension of PhIO in CH_2Cl_2 at 273 K, the EPR signal of complex **1** was transformed into another signal of Mn^{III}. The field position, shape and intensity of this signal markedly differ from those of **1** [compare Figures 3(*a*) and 3(*b*)]. Thus, a new complex of Mn^{III}, which is further denoted as complex **4**, is formed. Probably, complex **4** is the adduct Mn^{III}(salen)(OIPh). Recently, this adduct was detected by electrospray tandem mass spectrometry in the catalytic system **1** + PhIO in CH_2Cl_2.[20] Further studies are needed to support our assumption.

In conclusion, we have observed for the first time X-band EPR spectra of Mn^{III}(salen) complexes and demonstrated the applicability of EPR to studies of these practically important systems. ^{1}H NMR and EPR spectroscopic studies of the transformations of the Mn^{III}(salen) catalyst in the course of enantioselective epoxidation are in progress.

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