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# EPR and $^{1}$H NMR spectroscopic study of the Cr$^{III}$(salen)Cl catalysts

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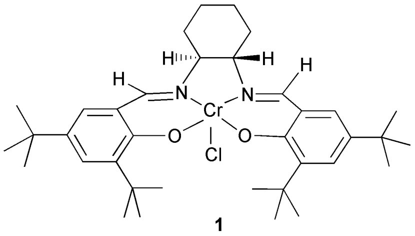
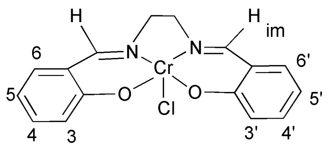
**An EPR and $^{1}$H, $^{2}$H NMR study of the Cr$^{III}$(salen)Cl type complexes was performed for the first time; the X-band EPR spectra of the $S$ = 3/2 Cr$^{III}$(salen)Cl complexes were interpreted using analytical expressions to reveal the $g$-factors and fine structure parameters, and assignment of the $^{1}$H and $^{2}$H NMR resonances was made.**

Cr$^{III}$(salen) complexes are widely employed as catalysts in alkene epoxidations,[1] asymmetric epoxidations,[2] kinetic resolution of epoxides,[3] alcohol oxidations[4] and enantioselective additions of allyl organometallic reagents to aldehydes.[5] The use of Cr$^{III}$(salen) complexes in epoxidations of unfunctionalised alkenes has several distinctive features compared to Mn$^{III}$(salen) catalysts,[2b,6] namely, acceleration of the reaction (by orders of magnitude) by donor additives (pyridine-$N$-oxide, triethylphosphine oxide, *etc.*),[1c] and the interesting fact that the chromium-salen system is more suitable for epoxidation of $E$-alkenes, whereas the manganese-salen one is best for $Z$-alkenes.[1]

To elucidate the mechanisms of the Cr$^{III}$(salen) catalysed reactions, it is important to monitor the catalyst transformations in the course of the reactions and hence to obtain spectral information about the catalyst itself. In this work, we report the first EPR and $^{1}$H NMR data on three Cr$^{III}$-(salen)Cl complexes, where salen = ($S$,$S$)-(+)-$N$,$N'$-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (**1**), salen = $N$,$N'$-bis(salicylidene)-1,2-ethylenediamine (**2**), salen = racemic $N$,$N'$-bis(3,4,5,6-tetra-deuterosalicylidene)-1,2-cyclohexanediamine (**3**).



**1**



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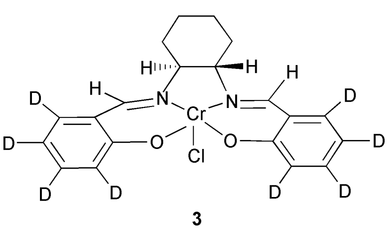

**3**

EPR spectroscopy has been successfully applied to the study of Cr(III) complexes.[7] The EPR spectra are interpreted based on the spin Hamiltonian

$$H = \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) + D[\{S_z^2 - 1/3S(S+1)\} + (E/D)(S_x^2 - S_y^2)]$$

where $S$ is the electronic spin, $D$ and $E/D$ are the usual axial and rhombic zero-field parameters.[8] EPR spectra of complexes **1**–**3** are collected in Fig. 1a–c. The observed $g$ values, $g \approx 4$ and 2, are typical of an electronic spin $S$ = 3/2, with moderately large zero field splitting $D$ and small rhombicity $E$ ($D > h\nu$, $E/D \approx 0$).[8b] In the limiting case of $D \gg h\nu$, $E = 0$, transitions between $|-3/2\rangle \leftrightarrow |-1/2\rangle$ ($g > 2$), $|-1/2\rangle \leftrightarrow |1/2\rangle$ ($g \approx 2$) and $|1/2\rangle \leftrightarrow |3/2\rangle$ ($g < 2$) levels of two Kramers doublets $|\pm3/2\rangle$, $|\pm1/2\rangle$ are expected.[8c] The weak signal at $g \approx 5.6$ is assigned to the almost forbidden "$\Delta m = 3$" transition within the $|\pm3/2\rangle$ Kramers doublet.[7a]

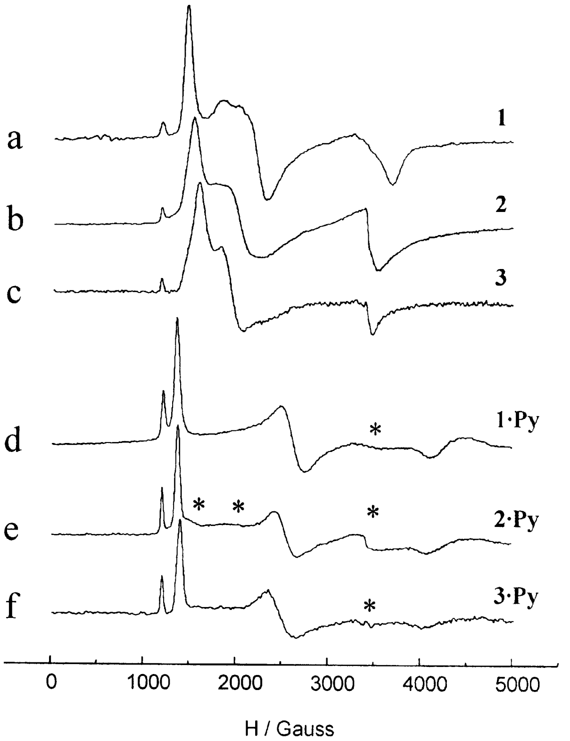

**Fig. 1** X-Band EPR spectra (77 K) of frozen 0.05 M solutions of Cr(III) complexes: (a) complex **1** in CH$_2$Cl$_2$; (b) complex **2** in DMF–toluene mixed solvent; (c) complex **3** in DMF–toluene mixed solvent. X-Band EPR spectra (77 K) of frozen 0.03 M solutions of Cr(III) complexes: (d) complex **1** in CH$_2$Cl$_2$ + pyridine (0.3 M); (e) complex **2** in DMF–toluene mixed solvent + pyridine (4.0 M); (f) complex **3** in DMF–toluene mixed solvent + pyridine (3.3 M). Spectrometer frequency 9.3 GHz; microwave power, 200 mW; modulation frequency, 100 kHz; modulation amplitude, 10 G; gain, 1 × 10$^4$.

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**Table 1** Best fit fine-structure parameters for the complexes **1**–**3** and **1**·Py–**3**·Py[a]

| | **1** | **2** | **3** | **1**·Py | **2**·Py | **3**·Py |
|---|---|---|---|---|---|---|
| $S$ | 3/2 | 3/2 | 3/2 | 3/2 | 3/2 | 3/2 |
| $g_{xx}$ | 1.95 | 1.96 | 1.96 | 1.95 | 1.96 | 1.95 |
| $g_{yy}$ | 1.95 | 1.96 | 1.96 | 1.95 | 1.96 | 1.95 |
| $g_{zz}$ | 1.95 | 1.97 | 1.96 | 1.97 | 1.97 | 1.95 |
| $D$/cm$^{-1}$ | 0.80 | 0.70 | 0.70 | 0.67 | 0.60 | 0.65 |
| $E$/cm$^{-1}$ | 0.108 | 0.063 | 0.042 | 0.150 | 0.119 | 0.120 |

[a] The fine-structure parameters for the complexes reproduced well the observed resonance fields for the canonical axes for the $|-3/2\rangle \leftrightarrow |-1/2\rangle$, $|-1/2\rangle \leftrightarrow |1/2\rangle$ and $|1/2\rangle \leftrightarrow |3/2\rangle$ transitions; however, the predicted field position for the forbidden low field transition within the $|\pm3/2\rangle$ doublet was generally underestimated by 10–25 G.

In practical epoxidations, donor ligand additives are employed as activators.[1c,2] The effect of donor additive (pyridine) on the EPR spectra was examined. It was found that upon addition of pyridine, the spectra shown in Fig. 1a–c are converted into those in Fig. 1d–f, indicating formation of new Cr$^{\mathrm{III}}$(salen) complexes upon complexation of one pyridine molecule per molecule of complexes **1**–**3** to form the respective adducts **1**·Py, **2**·Py and **3**·Py. In Fig. 1, lines of residual complex **2** are marked with asterisks.

To obtain the true $g$-factor values and fine structure parameters, $E$ and $D$, computational spin-Hamiltonian simulations,[7a] numerical calculations of the field and the probabilities of the transitions,[9a] or exact analytical solutions of the fine-structure spin-Hamiltonian are applied.[9b] The parameters determined using the procedure reported in ref. 9*b* are presented in Table 1. In all cases, addition of pyridine caused an increase of the rhombicity, $E$, and a decrease of the axial zero field parameter, $D$, indicating noticeable structural changes upon complexation with pyridine.

Earlier, $^1$H NMR studies of a number of Mn$^{\mathrm{III}}$(salen)Cl complexes have been undertaken by Bryliakov *et al.*,[10a] however, NMR investigations of Cr(III) complexes are rather complicated due to the very high line widths which are caused by rather long electron–spin relaxation times[10b] (of the order of $10^{-10}$ s).[10c] That is why only approximate resonance positions and line widths can be obtained from the $^1$H NMR spectra of complexes **1**–**3** (Table 2). DMSO was chosen due to the sufficient solubility of all complexes in this solvent. Assignment of the NMR resonances to the particular protons (deuterons) was made based on comparison of their resonance positions in different complexes.

It is clearly seen that there are two sets of $^2$H signals for complex **3** in a 1 : 1 ratio that are assigned to deuterons 3–6 and 3′–6′, respectively (Fig. 2). The observed magnetic nonequivalence of 3–6 and 3′–6′ positions of the phenolic rings is indicative of the non-planar conformation of Cr$^{\mathrm{III}}$(salen) complexes in solution (*i.e.* twisted or folded). Actually, one can conclude that the broad lines of the phenolic protons of complexes **1** and **2** are superpositions of two individual peaks. Deuteration was used to improve the spectral resolution of the phenolic ring protons. Indeed, irrespective of the relaxation mechanism, line width (in Hz) must be proportional to the squared magnetogyric ratio of the nucleus.[10b] Therefore, one can expect that the $^1$H peaks must be $6.5^2$ times broader than respective $^2$H peaks. In practice, however, this ratio may not be the case (*ca.* 10 times in our case). Assignment of the $^2$H NMR peaks of complex **2** in the region of −5 to 10 ppm to the 3, 3′ and 6, 6′ deuterons was made based on the assumption of dipolar spin relaxation and hence on their line widths:[10b] the 3, 3′ deuterons are situated closer to the Cr atom, so their resonances are broader (*cf.* ref. 10*a*).

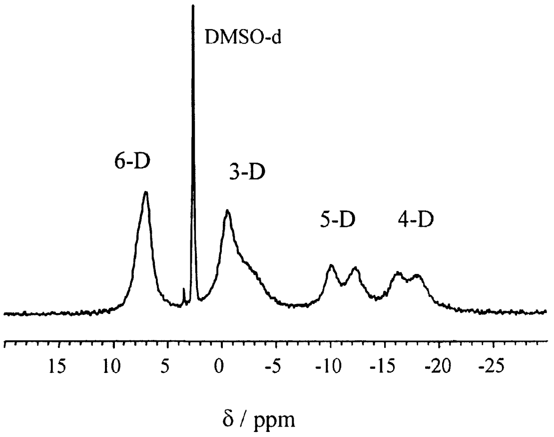

**Fig. 2** $^2$H NMR spectrum of a 0.05 M solution (DMSO, 20 °C) of complex **3**. The spectrum is a superposition of two sets (in a 1 : 1 ratio) of phenolic deuterons 3–6 and 3′–6′.

Some protons of the cyclohexanediamine ring in **1** and **3** as well as the protons of the ethylenediamine bridge in **2** and the imine protons in **1**–**3** can not be observed because of large line widths. Only some protons (most probably, those the most distant from the paramagnetic centre) were detected (see Table 2, "diamine protons").

In conclusion, the EPR and $^1$H, $^2$H NMR study of the practical multi-purpose chromium-salen catalysts has been performed for the first time. The fine-structure parameters for the $S$ = 3/2 Cr$^{\mathrm{III}}$(salen)Cl type complexes were determined, and assignment of their NMR signals was made. $^1$H and EPR spectroscopic studies of the catalyst transformation in the course of catalytic asymmetric ring openings and enantioselective epoxidations are in progress.

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**Table 2** $^1$H and $^2$H NMR shifts and line widths for complexes **1**–**3** (0.02 M solutions in DMSO, $T$ = 20 °C)

| | | Protons (deuterons) | | | | |
|---|---|---|---|---|---|---|
| Complex | | 3, 3′ | 4, 4′ | 5, 5′ | 6, 6′ | Diamine protons |
| **1** | | — | −18.7[a] (2.0[b]) | — | n/o[c] | −7.6 (1.0)<br>11.3 (2.0) |
| **2** | | −0.5 (1.0) | −18.1 (1.5) | −10.7 (1.2) | n/o[c] | n/o[d] |
| **3** | $^1$H | — | — | — | — | −6.8 (1.0)<br>−7.9 (1.0)<br>12.8 (2.0) |
| | $^2$H | −0.6 (0.06)<br>−2.5 (0.25) | −16.3 (0.11)<br>−18.1 (0.13) | −0.1 (0.10)<br>−12.3 (0.11) | 6.8 (0.06)<br>7.5 (0.07) | — |

[a] Hereinafter, paramagnetic shifts $\delta$, in ppm. Experimental uncertainty was ±0.5 ppm for $^1$H spectra and ±0.2 ppm for $^2$H spectra. [b] Hereinafter, line widths at half height, $\Delta\nu_{1/2}$, in kHz. Experimental uncertainty was ±0.4 kHz for $^1$H spectra and ±0.01 kHz for $^2$H spectra. [c] Not observed (hidden by intense solvent peaks). [d] Not observed (due to high line width).

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