# X-band perpendicular-mode EPR spectra of 'EPR-silent' manganese(III) porphyrins

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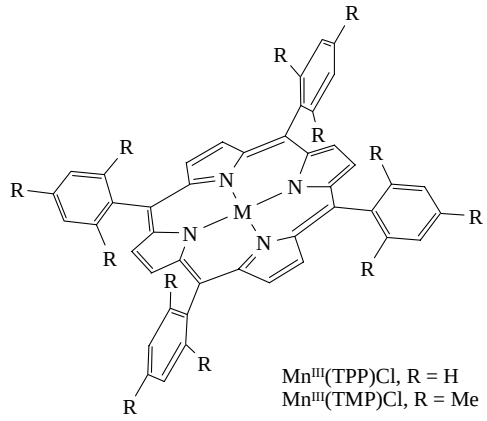
The X-band perpendicular-mode EPR spectra of manganese(III) porphyrins were detected for the first time.

In general, EPR spectroscopy at conventional microwave frequencies [X-band: ~9 GHz (0.3 $cm^{-1}$); Q-band: ~35 GHz (1.2 $cm^{-1}$)] is not applicable to 'EPR-silent' systems with integer-spin ground states where the zero-field splitting (zfs) is larger than the microwave quantum, in particular, where the zfs interaction approaches axial symmetry.[1] Thus, EPR studies of high-spin manganese(III) ($d^4$, $S = 2$) compounds are rather limited.[2–13]




**Scheme 1**

A weak EPR transition at $g \approx 8$ was observed for tris(acetylacetonato)manganese(III)[6] using X-band parallel- and perpendicular-mode EPR spectroscopy. We detected X-band perpendicular-mode EPR signals at $g \approx 8$ for Mn$^{III}$(salen) complexes.[7] Our assignment was confirmed by parallel-mode EPR spectroscopy.[8] Dual-mode EPR showed its utility for the study of Mn$^{III}$ in bioinorganic[9,10] and inorganic systems.[11–13]

In this work, we report that 'EPR-silent' manganese(III) porphyrins, which are widely used in biomimetic[14–17] and catalytic studies,[18–20] also display X-band perpendicular-mode EPR signals at $g \approx 8$–9 in frozen solutions at 77 K. The field positions of these signals are sensitive to the nature of donor molecules coordinated to the axial sites of manganese(III) porphyrins. EPR spectra for meso-tetraphenylporphyrinatomanganese(III) chloride, Mn(TPP)Cl, and 5,10,15,20-tetramesitylporphyrinatomanganese(III) chloride, Mn(TMP)Cl, and their adducts with pyridine and *N*-methylmorpholine *N*-oxide (NMO) are reported (Scheme 1).

The X-band perpendicular-mode EPR spectrum of a frozen 0.1 M Mn(TPP)Cl solution in $CH_2Cl_2$ at 77 K is shown in Figure 1(*a*).† The field position of the observed weak signal at $g = 7.4 \pm 0.2$ is close to those observed for tris(acetylacetonato)-manganese(III)[6] and Mn$^{III}$(salen)Cl[7] and is attributed to forbidden transitions within the $|\pm 2\rangle$ non-Kramers doublet. The signal at $g = 7.4$ cannot be assigned to Mn$^{II}$ species ($S = 5/2$), which may be present as impurities in Mn$^{III}$ preparations, because Mn$^{II}$ species display very intense resonance at $g = 2$ in addition to any other features at low field.

**Table 1** EPR spectroscopic data for manganese(III) complexes.

| Complex | Solvent | $g_{eff}$ | hfs/Gauss | Ref. |
|---|---|---|---|---|
| Mn(TPP)Cl | $CH_2Cl_2$ | 7.4±0.3 | —[a] | this work |
| Mn(TMP)Cl | $CH_2Cl_2$ | 7.4±0.3 | —[a] | this work |
| Mn(TPP)(Py)Cl | $CH_2Cl_2$/Py, 10:1 | 7.7±0.3 | 44±5 | this work |
| Mn(TPP)(NMO)Cl | $CH_2Cl_2$ + NMO[b] | 9.6±0.3 | —[a] | this work |
| Mn(acac)$_3$ | $CH_2Cl_2$ | 8.0±0.1 | 55±2 | 6 |
| Mn(salen)(NMO)Cl | $CH_2Cl_2$ + NMO[b] | 7.8±0.3 | 44±3 | 7 |

[a]Not observed. [b][NMO] = 1 mol $dm^{-3}$.

Addition of pyridine (1 mol $dm^{-3}$) to the sample shown in Figure 1(*a*) gives rise to a slight downfield shift of the observed peak ($g = 7.7 \pm 0.2$), and poorly resolved hyperfine lines from manganese separated by approximately 44 G can be distinguished. This hyperfine splitting (hfs) is similar to that observed for a Mn$^{III}$(salen) adduct with *N*-methylmorpholine *N*-oxide (Table 1).[7] Unexpectedly, the addition of *N*-methylmorpholine *N*-oxide (1 mol $dm^{-3}$) to the sample shown in Figure 1(*a*) provides a more pronounced downfield shift of the EPR signal [$g = 9.6 \pm 0.2$, Figure 1(*c*)]. Thus, the position of the observed forbidden resonance is sensitive to the nature of axial ligands in Mn$^{III}$ porphyrines. The EPR spectrum of Mn(TMP)Cl in $CH_2Cl_2$ at 77 K was identical to that of Mn(TPP)Cl.

In conclusion, we observed for the first time the X-band perpendicular-mode EPR spectra of manganese(III) porphyrins and their adducts with donor molecules.

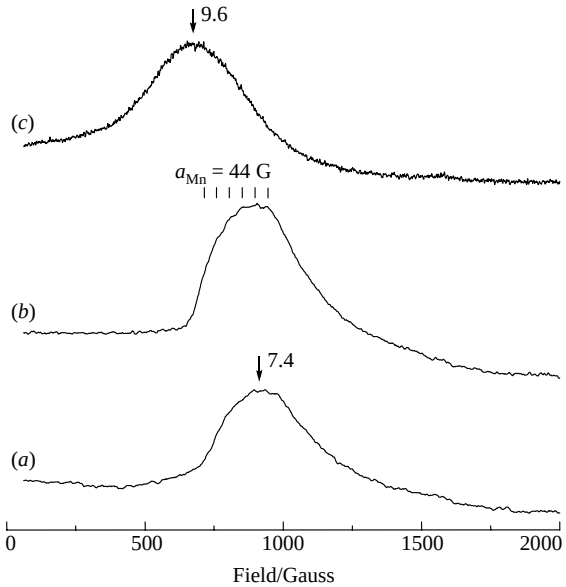



**Figure 1** X-band perpendicular-mode EPR spectra (77 K) of 0.1 M Mn(TPP)Cl solutions: (*a*) in $CH_2Cl_2$, (*b*) in $CH_2Cl_2$–Py (10:1) or (*c*) in $CH_2Cl_2$ with *N*-methylmorpholine *N*-oxide added.

† *General experimental details.* *N*-Methylmorpholine *N*-oxide, pyridine and $CH_2Cl_2$ from Aldrich were used. Free base porphyrins such as tetraphenylporphyrine (TPP)$H_2$[21] and tetramesitylporphyrin (TMP)$H_2$[22] were prepared in accordance with published procedures. Metallation to produce Mn$^{III}$TPP(Cl) and Mn$^{III}$TMP(Cl) was achieved by the Kruper method.[23] Perpendicular-mode EPR spectra were recorded in quartz tubes ($d = 5$ mm) at 77 K using a Bruker ER-200D X-band spectrometer. The dual EPR cavity furnished with the spectrometer was used. A periclase crystal (MgO) with $Mn^{2+}$ and $Cr^{3+}$ impurities served as a side reference, which was placed at the centre of the second compartment of the dual cavity ($Cr^{3+}$ exhibits a peak at $g = 1.9796$).

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