

A novel pentadentate ligand 2,6-bis[methoxybis(2-pyridyl)methyl]pyridine L for mononuclear iron(II) and manganese(II) compounds; synthesis and crystal structures of [FeL(MeCN)][ClO₄]₂ and [(MnL(H₂O))][ClO₄]₂

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A novel pentadentate ligand L is capable of stabilising Fe^{II} and Mn^{II} centres, the first of which gives a transient iron hydroperoxide species upon treatment with hydrogen peroxide.

Mononuclear iron and manganese centres are common in oxygenases and the synthesis of low molecular mass complexes that show structural and functional similarities to natural systems is of great current interest.^{1,2} An approach to novel biomimetic catalysts for selective oxygenations is based on the design of multidentate ligands that can accommodate low-valent iron^{1,2} or manganese^{1,3} and are capable of stabilising intermediates in the oxygenation cycles. We wish to present a unique ligand L with a fivefold pyridine donor set which is particularly effective for this purpose. This is demonstrated by the synthesis and structural characterisation of the corresponding iron [FeL(MeCN)][ClO₄]₂ **1** and manganese [MnL(H₂O)][ClO₄]₂ **2** complexes.

Ligand L was prepared in a three step procedure, from pyridine-2,6-dicarboxylic acid (Scheme 1). Treatment with SOCl₂ was followed by reaction of the acid chloride with 6 equiv. of 2-pyridyllithium. The resulting 2,6-bis[hydroxybis(2-pyridyl)methyl]pyridine was methylated to afford L.

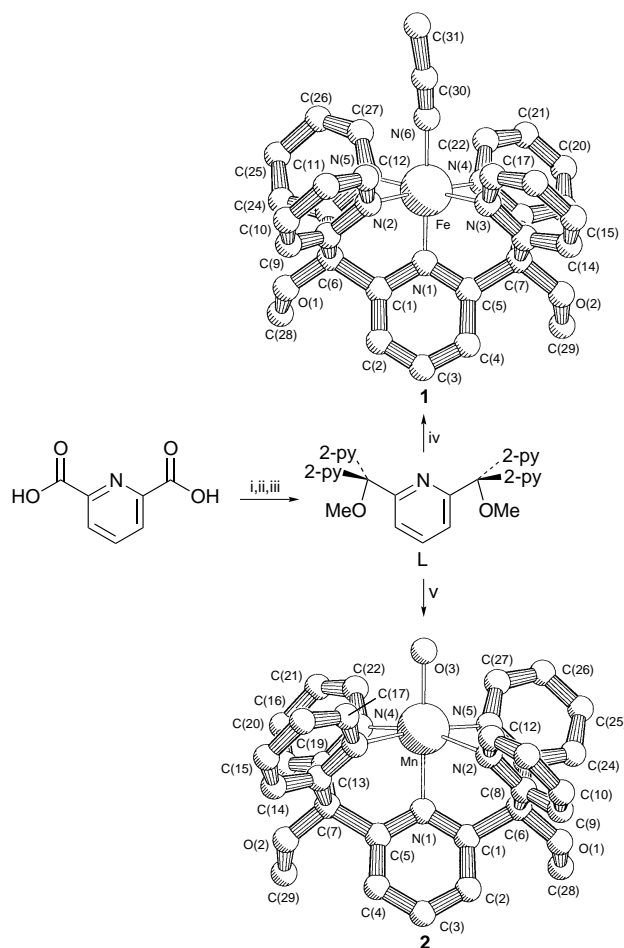
Complexation of L with Fe(ClO₄)₂·6H₂O in MeCN–CH₃OH (1 : 1) gave **1** in 86% yield. Red–brown crystals were obtained by slow diffusion of ethyl acetate into the product solution. Complex **1** is a low-spin iron(II) complex as deduced from its diamagnetic ¹H NMR spectrum[‡] and absence of EPR signals. Furthermore in acetonitrile the complex has an absorption maximum at 425 nm. Cyclic voltammetry of **1** in acetonitrile shows reversible oxidation at 1.21 V vs. SCE corresponding to the Fe^{III}–Fe^{II} couple.

The crystal structure of **1** shows a six-coordinate Fe^{II} centre surrounded by nitrogen atoms from four equatorial and one apical pyridine moieties.[§] The second apical position is occupied by an acetonitrile molecule. The four equatorial pyridine rings are not positioned perpendicular to the basal plane but are folded outwards to provide a cleft-type of arrangement. The Fe–N bond lengths to N(1), N(4), N(5) and N(6) of 1.93–2.00 Å are characteristic for a low-spin Fe^{II} centre.^{4–6} The Fe–N(2) and Fe–N(3) bond lengths of 2.08 Å are long for a low-spin iron(II) complex, which is probably due to the fact that the cleft formed by the four equatorial pyridine rings is slightly too large to accommodate a low-spin Fe^{II} with equal Fe–N distances.

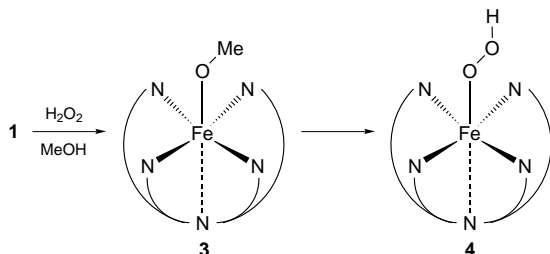
Treatment of **1** in methanol with an excess (100 equiv.) of hydrogen peroxide at 25 °C (Scheme 2) causes the appearance of a blue species (λ_{max} = 592 nm) with a half-life of 3 h.

The nature of this intermediate was examined by electrospay ionisation mass spectrometry (nozzle = 70 V). The results show that immediately after addition of H₂O₂ a prominent ion,

with a peak cluster at *m/z* 661 is formed which can be formulated as {[FeL(OCH₃)](ClO₄)}⁺ **3**.¶ This indicates initial oxidation of iron(II) complex **1** to an iron(III) species. In the course of the reaction with hydrogen peroxide an ion with *m/z* 663 is formed at the expense of **3** which corresponds to {[FeL(OOH)](ClO₄)}⁺ **4**.



Scheme 1 Synthesis of L, complexes **1** and **2** and X-ray crystal structures of the cations of **1** and **2**. Hydrogens have been omitted for clarity. *Reagents and conditions:* i, SOCl₂, reflux, 4 h; ii, BuⁿLi, 2-bromopyridine, thf; iii, NaH, MeI, thf; iv, Fe(ClO₄)₂·6H₂O, MeCN, MeOH; v, Mn(ClO₄)₂·6H₂O, MeCN. Selected interatomic distances (Å): for **2**: Fe–N(1) 1.927(8), Fe–N(2) 2.078(8), Fe–N(3) 2.076(9), Fe–N(4) 1.995(9), Fe–N(5) 1.957(8), Fe–N(6) 1.952(8). For **3**: Mn–O(3) 2.100(3), Mn–N(1) 2.223(3), Mn–N(2) 2.297(3), Mn–N(3) 2.248(3), Mn–N(4) 2.230(3), Mn–N(5) 2.214(3).



Scheme 2 Formation of the blue iron(II) hydroperoxide complex **4**

The assignment of the blue species as a hydroperoxide complex **4** is furthermore based on similar spectroscopic data as reported recently for an iron(III) hydroperoxide intermediate.^{5,6} It is also corroborated by the results from EPR measurements at 77 K which exhibit g values at 2.15, 2.13 and 1.98 indicative of a low-spin iron(III) species.^{2,5–7} Based on the available coordination site and the pentadentate nature of L an end-on hydroperoxide structure for **4** is proposed.

Preliminary investigations show that complex **1** is catalytically active in the oxidation of alkanols. For example, treatment of benzyl alcohol in acetone with 100 equiv. of H_2O_2 in the presence of **1** gave a clean and fast conversion to benzaldehyde (65 equiv. with respect to **1** within 0.5 h).^{||}

Treatment of a solution of L in acetonitrile with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ followed by vapour diffusion of diethyl ether resulted in greyish crystals of $[\text{MnL}(\text{H}_2\text{O})][\text{ClO}_4]_2$ **2** (35% yield). Complex **2** shows no absorptions in the visible spectrum which points to a high-spin manganese(II) complex.^{3,8}

Electrospray ionisation mass spectrometry (nozzle = 70 V) affords prominent peaks at m/z 265, 629, corresponding to the ions $[\text{MnL}]^{2+}$ and $\{[\text{MnL}](\text{ClO}_4)\}^+$, respectively. The crystal structure of **2** exhibits similar features as found for **1** including six-coordination of manganese with four pyridines.[§] In contrast to complex **1**, one apical position is occupied by a water molecule, which donates two hydrogen bonds to the two independent ClO_4^- anions. The Mn–N bond lengths of 2.21–2.30 Å are typical for the Mn–N(pyridyl) distances observed in six-coordinated manganese(II) complexes.^{3,8} The Mn–O distance is 2.10 Å.

In conclusion, a new pentadentate ligand L has been designed. The pentadentate nature of L is evident from the structures of **1** and **2** leaving a sixth coordination site free to accommodate weakly bonded ligands such as acetonitrile and water. This ligand is effective in the formation of iron(II) and manganese(II) complexes and capable of stabilising a transient hydroperoxide species. Catalytic oxidation experiments with these new complexes are in progress.

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Footnotes and References

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‡ ^1H NMR (200 MHz, CD_3CN , 25 °C): δ 2.11 (m, 3 H, MeCN), 4.04 (s, 6 H, OCH_3), 8.01 (m, 15 H, py), 9.94 (m, 4 H, py).

§ *Crystal data*: for **2**, $\text{C}_{31}\text{H}_{28}\text{Cl}_2\text{FeN}_6\text{O}_{10}$, $M_r = 771.35$, red–brown, block-shaped crystal ($0.2 \times 0.2 \times 0.1$ mm), monoclinic, space group $P2_1$ (no. 4), $a = 9.751(2)$, $b = 19.326(5)$, $c = 9.7986(17)$ Å, $\beta = 101.427(17)^\circ$, $U = 1809.9(7)$ Å³, $Z = 2$, $D_c = 1.415$ g cm^{–3}, $F(000) = 792$, $\mu(\text{Mo-K}\alpha) = 6.3$ cm^{–1}, 3495 reflections measured, 3293 independent, ($1.05 < \theta < 25.00^\circ$, ω scan, $T = 150$ K, Mo-K α radiation, graphite monochromator, $\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 Turbo diffractometer on rotating anode. Data were corrected for L_p effects and for linear decay of 3% of the reference reflections, but not for absorption. The structure was solved by automated Patterson methods (DIRDIF96). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-96); no observance criterion was applied during refinement. Electron density in a disordered solvent area (164 Å³, 47.9 e per asymmetric unit) was taken into account in the refinement via PLATON/SQUEEZE. Where relevant, data cited above are given without disordered solvent contribution. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. Refinements of a racemic twin model resulted in slightly lower wR_2 values and a component ratio of 0.84(10):0.16. Refinements converged at a final wR_2 value of 0.1674, $R_1 = 0.0669$ [for 2282 reflections with $F_\sigma > 4\sigma(F_\sigma)$], $S = 0.985$, for 455 parameters. A final difference Fourier showed no residual density outside -0.76 and 0.59 e Å^{–3}.

¶ For **3**, $\text{C}_{29}\text{H}_{27}\text{Cl}_2\text{MnN}_5\text{O}_{11}$, $M_r = 747.40$, greyish, block-shaped crystal ($0.4 \times 0.2 \times 0.1$ mm), monoclinic, space group $P2_1/c$ (no. 14), $a = 12.5605(12)$, $b = 12.8173(12)$, $c = 19.3461(17)$ Å, $\beta = 93.360(8)^\circ$, $U = 3109.2(5)$ Å³, $Z = 4$, $D_c = 1.597$ g cm^{–3}, $F(000) = 1532$, $\mu(\text{Mo-K}\alpha) = 6.7$ cm^{–1}, 8433 reflections measured, 7119 independent, ($1.06 < \theta < 27.50^\circ$). Data collection and handling were performed as described for compound **2**. The reference reflections displayed a linear decay of 2%. The structure was solved by automated Patterson methods (SHELXS-86). The water hydrogen atoms were located on a Fourier map and subsequently included in the refinement. Refinement converged at a final wR_2 value of 0.1331, $R_1 = 0.0564$ [for 4676 reflections with $F_\sigma > 4\sigma(F_\sigma)$], $S = 1.021$, for 462 parameters. A final difference Fourier showed no residual density outside -0.66 and 0.50 e Å^{–3}. CCDC 182/491.

¶¶ A related iron(III) methoxy species was observed by ES–MS for $[\text{FeL}'(\text{MeCN})][\text{ClO}_4]_2$ [$\text{L}' = N,N$ -bis(2-pyridylmethyl)- N -bis(2-pyridyl)methylamine] and the crystal structure of the corresponding methoxy complex was recently solved; manuscript is in preparation.

¶¶ For selective catalytic oxidation of alkanols to aldehydes with manganese complexes and hydrogen peroxides, see ref. 9.

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