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)

De Vries, Maartje E.; la Crois, Rene M.; Roelfes, Gerard; Kooijman, H.; Spek, A.L.; Hage, R.; Feringa, B.L.

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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 \([\text{FeL(MeCN)}][\text{ClO}_4]\)\(_2\) and \([\text{MnL(H}_2\text{O)}][\text{ClO}_4]\)\(_2\)

Maartje E. de Vries,\(^a\) Rene M. La Crois,\(^a\) Gerard Roelfes,\(^a\) Huub Kooijman,\(^b\) Anthony L. Spek,\(^c\) Ronald Hage\(^e\) and Ben L. Feringa\(^{a*}\)

\(^a\) Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
\(^b\) Bijvoet Centre for Biomolecular Research, Crystal and Structural Chemistry, University of Utrecht, Padulalaan 8, 3584 CH Utrecht, The Netherlands
\(^c\) Unilever Research Laboratory Vlaardingen, PO Box 144, 3130 AC Vlaardingen, The Netherlands

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\([\text{FeL(MeCN)}][\text{ClO}_4]\)\(_2\) \(1\) and manganese \([\text{MnL(H}_2\text{O)}][\text{ClO}_4]\)\(_2\) \(2\) complexes.

Ligand \(L\) was prepared in a three step procedure, from pyridine-2,6-dicarboxylic acid (Scheme 1). Treatment with SOCl\(_2\) was followed by reaction of the acid chloride with 6 equiv. of 2-pyridyllithium. The resulting \(2,6\)-bis[methoxybis(2-pyridyl)methyl]pyridine was methylated to afford \(L\).

Complexation of \(L\) with \(\text{Fe(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O in MeCN–CH}_3\text{OH (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 1\(H\) NMR spectrum\(^\text{‡}\) and absence of EPR signals. Furthermore in acetonitrile the complex has an absorption maximum at 425 nm. Cyclic voltammetry of \(\text{FeIII–FeII couple.}\)

The crystal structure of \(1\) shows a six-coordinate Fe\(^{II}\) centre surrounded by nitrogen atoms from four equatorial and one apical pyridine moieties.\(^\text{§}\) 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 (\(\lambda_{\text{max}} = 592\) nm) with a half-life of 3 h.

The nature of this intermediate was examined by electrospray ionisation mass spectrometry (nozzle = 70 V). The results show that immediately after addition of H\(_2\)O\(_2\) a prominent ion, with a peak cluster at \(m/z\) 661 is formed which can be formulated as \([\text{FeL(OCH}_3\text{)}][\text{ClO}_4]\)\(^+\). 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 \([\text{FeL(OOH)}][\text{ClO}_4]\)\(^+\).

\(\text{Scheme 1 Synthesis of L, complexes 1 and 2 and X-ray crystal structures of the cations of 1 and 2. Hydrogens have been omitted for clarity. Reagents and conditions: i, SOCl}_2, \text{reflux, 4 h; ii, Bu}_4\text{Li, 2-bromopyridine, thf; iii, NaH, Me, thf; iv, Fe(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O, MeCN, MeOH; v, Mn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O, MeCN. Selected interatomic distances (Å): for 1, Fe–N(1) 1.927(8), Fe–N(2) 2.086(8), Fe–N(3) 2.076(8), Fe–N(4) 1.995(8), Fe–N(5) 1.957(8), Fe–N(6) 1.952(9); for 2, Mn–N(1) 2.185(9), Mn–N(2) 2.310(9), Mn–N(3) 2.340(9), Mn–N(4) 2.297(9), Mn–N(5) 2.214(3).}\)
The assignment of the blue species as a hydroperoxide complex is further based on similar spectroscopic data as reported recently for an iron(III) hydroperoxide intermediate. 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. 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 H₂O₂ in the presence of 1 gave a clean and fast conversion to benzaldehyde (65 equiv. with respect to MeOH). 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. 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 H₂O₂ in the presence of 1 gave a clean and fast conversion to benzaldehyde (65 equiv. with respect to MeOH). 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. Based on the available coordination site and the pentadentate nature of L an end-on hydroperoxide structure for 4 is proposed.

Electrospray ionisation mass spectrometry (nozzle = 70 V) for FeL, [FeL(H₂O)][ClO₄]²⁻ and [FeL(ClO₄)]⁺, respectively. The crystal structure of 2 exhibits similar features as found for 1 including six-coordinate of manganese with four pyridines in the equatorial positions. In contrast to complex 1, one apical position is occupied by a water molecule, which donates two hydrogen bonds to the two independent ClO₄⁻ 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. 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

* E-mail: feringa@chem.rug.nl
† Address correspondence concerning crystallography to this author.
‡ H NMR (200 MHz, CD₃CN, 25 °C): δ 2.11 (m, 3H, MeCN), 4.04 (s, 6 H, OCH₃), 8.01 (m, 15 H, py), 9.94 (m, 4 H, py).
§ Crystal data: for 2, C₃₂H₂₆Cl₂MnNO₆, Mᵣ = 771.35, red–brown, block-shaped crystal (0.2 × 0.2 × 0.1 mm), monoclinc, space group P2₁/c (no. 14), a = 12.5605(12) Å, b = 12.8173(12) Å, c = 19.3461(17) Å, β = 93.360(8)°, U = 3109.2(5) Å³, Z = 4, Dₚ = 1.597 g cm⁻³, F(000) = 1532, μ(Mo-Kα) = 6.7 cm⁻¹, 8433 reflections measured, 7119 independent, (1.06 < θ < 27.50°). Data collection and unit cell refinement were performed on a Rietveld program (CCDC 182/491). 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 wR₁ value of 0.1674, R₁ = 0.0669 [for 2282 reflections with F(0) > 4σ(Fo)]. 3 S. J. Lippard and M. B. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994; Bioinorganic Catalysis, ed. J. Reedijk, M. Dekker, New York, 1993; A. L. Feig and S. J. Lippard, Chem. Rev., 1994, 94, 759.

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