A Manganese Tris Quinone Oximato Pair revealing New Structures and Magnetic Properties in $Mn^{III,II}$ Chemistry

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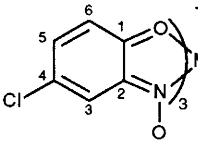
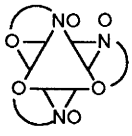
The synthesis and isomerism of the first tris-chelated low-spin Mn^{III} (**1a**) and Mn^{II} (**1b**) pair of complexes $[MnL_3]^{0,-}$, of the 4-chloro-*o*-benzoquinone oxime ligand HL is described; MnL_3 has strong preference for *mer*-geometry but *mer*- and *fac*-isomers coexist in solution as well as in the crystal lattice of the $[Et_4N]^+$ salt of $[MnL_3]^-$.

The title pair of complexes, $[Mn^{III}L_3]$ **1a** and $[Et_4N][Mn^{II}L_3]$ **1b**, provide the first examples of several features in manganese chemistry: (*i*) low-spin configuration for both Mn^{III} and Mn^{II} in identical chelated environments, (*ii*) low-spin Mn^{III} with nonporphyrinic N,O coordination and (*iii*) oxidation state-selective tris-chelate geometrical isomerism for Mn^{III} and Mn^{II} including a remarkable Mn^{II} lattice in which two isomers coexist in an ordered 1:1 proportion. Complex **1a** was synthesised by the reaction of $[Mn(MeCO_2)_3]\cdot 2H_2O$ with the free ligand[1] in methanol. Exhaustive electrolytic reduction of **1a** in MeCN at 0.0 V *vs.* saturated calomel electrode (SCE) in the presence of $[Et_4N]Cl$ afforded **1b**.†[2]



$[MnL_3]^0$ **1a**, $z = 0$
$[MnL_3]^-$ **1b**, $z = 1-$, cation = $[NEt_4]^+$



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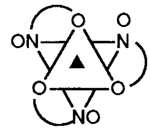

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Magnetic moments (μ_{eff}, 300 K) correspond to a low-spin configuration: **1a**, 2.98 (solid) and 3.10 μ_B ($CDCl_3$ solution); **1b**, 1.77 and 1.80 μ_B. Low-spin Mn^{III} ($S = 1$)[3] and Mn^{II} ($S = 1/2$)[4,5] complexes are not common and CN^- has been the only ligand affording tractable species for both the oxidation states[6] as in the pair $[Mn(CN)_6]^{3-,4-}$. We now have the first chelated pair in the form of $[MnL_3]^{0,-}$. Our findings may have a bearing with respect to the S_2 state of photosystem II.[7]

The isomerism of **1a** is revealed by 270 MHz ^1H NMR spectroscopy in $CDCl_3$. Three equally intense contact-shifted signals occur for each of three types of ring protons (3-H: δ 17.40, 10.60 and 9.67; 5-H: δ 41.60, 36.86 and 24.29; 6-H: δ −5.4, −9.15 and −24.28; 305 K). No other resonances are observed. The 5-H region of the spectrum is shown in Fig. 1(*a*). Evidently **1a** has virtually exclusive *mer*-geometry (**2**, inequivalent ligands) rather than *fac*-geometry (**3**, equivalent ligands); the equilibrium concentration of the *fac*-form is very small (see below).

Unlike **1a**, complex **1b** afforded single crystals which are unique in having an ordered array of equal proportions of *fac*- and *mer*-isomers within the same lattice. The asymmetric unit of the complex is thus $[Et_4N]_2$[*mer*-MnL_3][*fac*-MnL_3]. The X-ray structures‡ of the two isomers are shown in Fig. 2. The average Mn–N and Mn–O distances [1.93(2) and 1.97(1) Å respectively] are shorter (contraction of metal due to spin-pairing)[5,9] than those usually observed (2.1–2.3 Å) in high-spin Mn^{II} ($S = 5/2$). The intraligand distances are similar to those of other quinone oxime complexes and a nitrosophenolate resonance contribution is probably present.[10]

The two isomers of **1b** also coexist in solution as revealed by voltammetry [Fig. 1(*b*)]. From peak height data the equilibrium constant [*mer*]/[*fac*] is 2.2 (CH_2Cl_2, 256 K). From electrochemical studies, not elaborated here, the corresponding equilibrium constant for **1a** was estimated to be *ca.* 10^4.

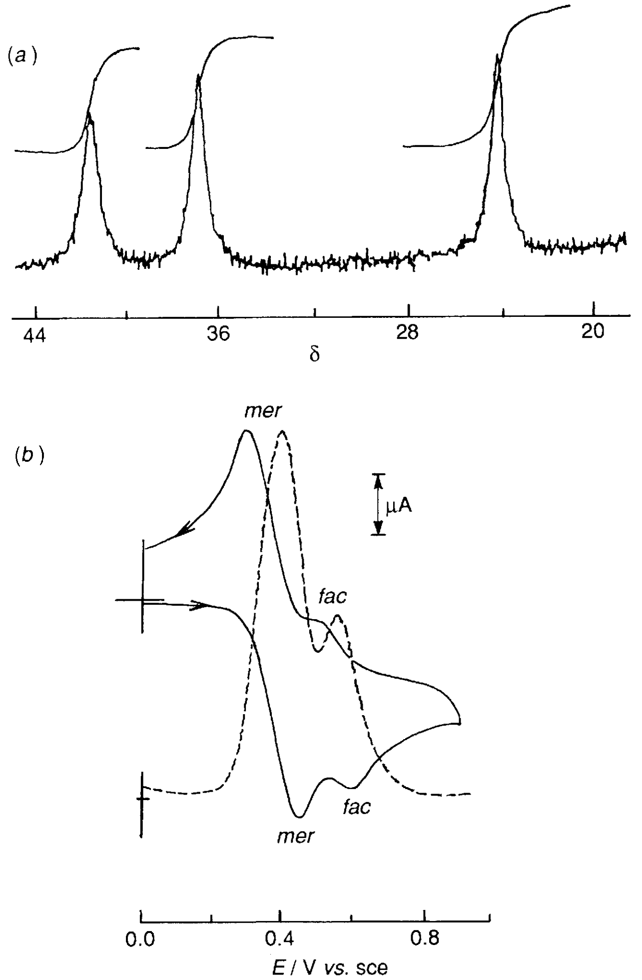

Fig. 1 (*a*) ^1H NMR signals for the 5-H proton of $[MnL_3]$ in $CDCl_3$ at 305 K. (*b*) Cyclic (cv) (———) and differential pulse (dpv) (- - -) voltammogram of $[MnL_3]^-$ in dichloromethane (0.1 mol dm^{-3} Et_4NClO_4) at 256 K. The marked current range is 5 μA (cv) and 10 μA (dpv).

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† Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **1b**: $C_{26}H_{29}N_4O_6Cl_3Mn$, $M = 654.8$, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 12.205(6)$, $b = 13.645(9)$, $c = 18.076(10)$ Å, $\alpha = 91.04(5)$, $\beta = 94.07(4)$, $\gamma = 96.06(4)^\circ$, $V = 2985(3)$ $Å^3$, $T = 296$ K, $D_c = 1.457$ g cm^{-3}, μ(Mo-Kα) = 7.39 cm^{-1}, crystal dimensions 0.14 × 0.19 × 0.28 mm^3. Data were collected in the range $2.0 \leqslant 2\theta \leqslant 43^\circ$ by the ω-scan method on a Nicolet R3m/V four-circle diffractometer. Correction of Lorentz–polarization effects and absorption (empirically) was done. Out of 6847 unique reflections, 2342 satisfying $F > 5.6\sigma(F)$ were used for structure solution (Patterson and difference Fourier methods). Only metal, chlorine and coordinated oxygen atoms were made anisotropic. The total number of variables refined was 391. Hydrogen atoms were included at calculated positions ($U = 0.08$ $Å^2$). The crystal was relatively weakly diffracting and the peak profiles were broad. Only moderate precision could therefore be achieved. The structure refined to $R = 8.80\%$ and $R_w = 8.88\%$. The highest difference fourier peak was 0.46 e $Å^{-3}$. All calculations were done using the SHELXTL-Plus program[8] package. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

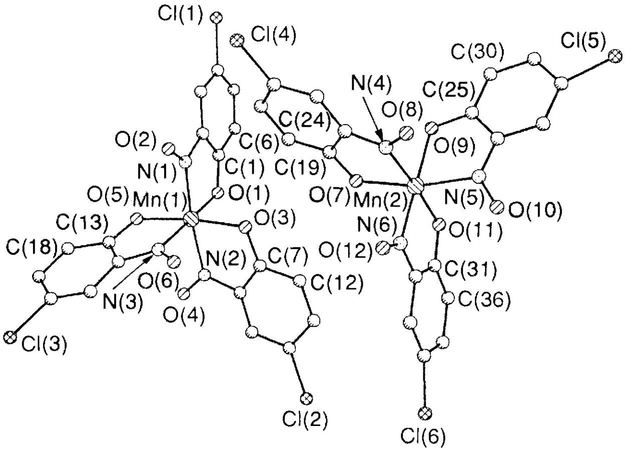

Fig. 2 Perspective views of *mer*- and *fac*-[MnL$_3$]$^-$ in the lattice of [Et$_4$N][MnL$_3$]. Selected distances (Å) and angles (°): Mn(1)–O(1), 1.963(11); Mn(1)–O(3), 1.920(11); Mn(1)–O(5), 1.910(11); Mn(1)–N(1), 1.911(15); Mn(2)–N(2), 1.961(13); Mn(1)–N(3), 1.950(14); Mn(2)–O(7), 1.945(12); Mn(2)–O(9), 2.096(13); Mn(2)–O(11), 2.012(14); Mn(2)–N(4), 1.947(16); Mn(2)–N(5), 1.934(17); Mn(2)–N(6), 1.902(19); O(1)–Mn(1)–O(3), 92.8(5); O(1)–Mn(1)–O(5) 94.0(5); O(1)–Mn(1)–N(1), 82.1(6); O(1)–Mn(1)–N(2), 94.0(5); O(1)–Mn(1)–N(3), 174.2(5); N(1)–Mn(1)–N(2), 173.0(6); O(7)–Mn(2)–O(9), 85.7(5); O(7)–Mn(2)–O(11), 92.7(5); O(7)–Mn(2)–N(4), 82.5(6); O(7)–Mn(2)–N(5), 166.6(6); O(7)–Mn(2)–N(6), 92.3(6).

The structural preferences of Mn^{III} (d^4) and Mn^{II} (d^5) are thus different. Oxidation state-selective isomer populations in solution have also been observed among Fe(d^5, d^6),[11] Ni(d^7, d^8)[1] and other[12] 3d quinone oximato complexes.

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