Chelated Paraquinone Co-ordination in Bis(phthiocolato)bis(pyridine)manganese(II)

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The hydroxyparaquinone complex bis(phthiocolato)bis(pyridine)manganese(II) has been synthesized and characterized spectrally and by *X*-ray crystallography.

Quinone complexes of manganese have proved to be of considerable interest for their ability to undergo intramolecular metal–ligand electron transfer.[1] Photolysis of solutions containing $Mn_2(CO)_{10}$ and 3,5-di-t-butyl-1,2-benzoquinone (dbsq) produced the green bis(3,5-di-t-butylsemiquinone)manganese(II) tetramer, $[Mn(dbsq)_2]_4$.[2] Treatment of the tetramer with pyridine (py) resulted in formation of the monomeric bis(pyridine) adduct.[1] In the solid state this complex containins Mn^{IV} chelated by quinone ligands in the di-t-butylcatecholate (dbcat) form, $Mn^{IV}(py)_2(dbcat)_2$. However, in toluene solution at room temperature purple crystals of the Mn^{IV} complex gave a green solution of $Mn^{II}(py)_2(dbsq)_2$. This compound is related to the Mn^{IV} complex by transfer of two electrons from the reduced catecholate ligands to the oxidized metal. Magnetic and spectral studies have been used to study the equilibrium (1) between the Mn^{II} and Mn^{IV} forms.[1]

$$Mn^{IV}(py)_2(dbcat)_2 \rightleftharpoons Mn^{II}(py)_2(dbsq)_2 \qquad (1)$$

Electron transfer reactions which occur during energy conversion processes in biological systems sometimes involve interaction between the metal of a metalloprotein and a paraquinone or quinoid electron acceptor.[3] The co-ordination chemistry of paraquinones has not been extensively developed, however,[4] and in this report we describe the use of *ortho* functionalized paraquinones as chelating agents. The aim of this project is to determine whether paraquinones exhibit the same facile electron transfer properties to metal ions as found for orthoquinone ligands. Phthiocol (2-methyl-3-hydroxy-1,4-naphthoquinone) (phth), a naturally occurring pigment associated with bacteria grown on synthetic culture media, was used in this particular study.[5] An aqueous solution of manganese(II) acetate treated with two equivalents of phthiocol under an inert atmosphere produced a dark red-brown precipitate of $Mn(phth)_2(H_2O)_2$. The complex shows strong i.r. absorptions at 1650, 1600, 1270, and 1215 cm^{-1}, bands in the u.v.–visible region at 505(ε 6286) and 330(7500) nm, and a magnetic moment of 5.90 μ_B indicating the presence of high spin Mn^{II}. Upon treatment with pyridine, the bis(pyridine) complex $Mn(phth)_2(py)_2$ formed quantitatively. This complex is closely related to the 3,5-di-t-butylsemiquinone complex described above. Crystals of $Mn(phth)_2(py)_2$ were grown from diethyl ether–pyridine solution and were used for crystallo-

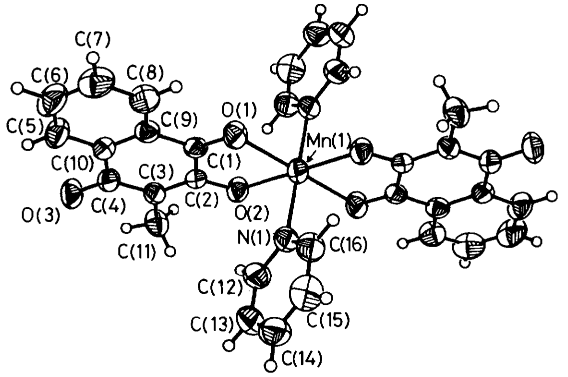

Figure 1. ORTEP diagram of $Mn(phth)_2(py)_2$. Mn–O(1) 2.230(4), Mn–O(2) 2.100(3), Mn–N(1) 2.295(4), C(1)–O(1) 1.217(6), C(2)–O(2) 1.298(5), C(4)–O(3) 1.240(6), C(1)–C(2) 1.495(7), C(2)–C(3) 1.366(6), C(3)–C(4) 1.433(7) Å.

graphic investigation.† The complex molecule shown in Figure 1 is located about a crystallographic inversion centre in the unit cell. Quinone C–O bond lengths of 1.217(6) Å for the C(1)–O(1) bond and 1.240(6) Å for C(4)–O(3) are significantly different and, with the C(2)–O(2) length of 1.298(5) Å, appear to reflect conjugation over the O(2)–C(2)–C(3)–C(4)–O(3) region of the ligand. Bond lengths to the manganese ion are typical of Mn^{II} values and differ significantly from the Mn^{IV} values of 1.853(2) for Mn–O and 2.018(3) Å for Mn–N found for *trans*-$Mn(py)_2(dbcat)_2$.[1] In dimethylformamide solution at room temperature the complex shows spectral bands which are similar to $Mn(phth)_2(H_2O)_2$. The electronic structure of the complex fails to show the solvent and thermal dependence found for $Mn(dbcat)_2(py)_2$. It remains as an interesting and unique example of paraquinone co-ordination to Mn^{II}, however. Recent evidence indicates that the manganese centres of the photosynthetic water oxidation enzyme are associated with a redox-active ligand which facilitates electron-transfer.[6] Plastoquinone has been identified as a component of the water oxidation system and has been suggested as a potential ligand for the manganese centres.[7]

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† *Crystal data:* $C_{32}H_{24}MnN_2O_6$, monoclinic, space group *C2/c*, a = 12.400(3), b = 18.055(5), c = 12.851(2) Å, β = 109.09(2)°, U = 2719 $Å^3$, D_c = 1.44 g cm^{-3}, Z = 4, Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by heavy-atom techniques and refined using 1192 unique, observed [$F > 6\sigma(F)$] reflections. R = 0.044, R_w = 0.060, GOF = 1.02. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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