Synthesis and Molecular Structure of an Unsymmetric Dimanganese(II) Carboxylato Complex

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A dimanganese(II) complex $[\mathrm{Mn\{HB(3,5\text{-}Pr^i_2pz)_3\}(\mu\text{-}OBz)_3Mn(3,5\text{-}Pr^i_2pzH)_2}]$ **1**† has been synthesized from a mixture of $[\mathrm{Mn(Cl)\{HB(3,5\text{-}Pr^i_2pz)_3\}}]$, 3,5-$\mathrm{Pr^i_2pzH}$, $\mathrm{MnCl_2{\cdot}4H_2O}$ and NaOBz; X-ray analysis establishes the unsymmetric coordination environment of each manganese ion with a structurally unique bridging unit consisting of three carboxylate groups.

Several proteins are thought to contain a polynuclear manganese centre bridged with carboxylates.[1–6] It is well established that manganese ions easily polymerize and form dinuclear, trinuclear and higher nuclear complexes in the presence of carboxylates. Accordingly, a variety of polynuclear manganese carboxylato complexes are known[1,2,7] and some of them serve as structural analogues for the manganese sites in the oxygen evolving complex of PS II,[1,2] ribonucleotide reductase[3] and manganese catalase.[5,6] Recently (μ-carboxylato)$_n$ units, where n = 1–3, were pointed out as a plausible bridging structure of the dimanganese(II) site in the manganese substituted ribonucleotide reductase[4] or the fully reduced manganese catalase.[6] Some dinuclear manganese(II) complexes having (μ-carboxylato)$_{2-4}$ units have been reported.[1,8,9] All these complexes, however, adopt a symmetric structure. Here we report the synthesis and characterization of an unsymmetric dimanganese(II) complex which possesses a structurally unique (μ-carboxylato)$_3$ unit, although its biological relevance is not certain.

The anaerobic reaction of $[\mathrm{Mn(Cl)\{HB(3,5\text{-}Pr^i_2pz)_3\}}]$† (0.71 g, 1.0 mmol), with 3,5-$\mathrm{Pr^i_2pzH}$ (0.76 g, 5.0 mmol), $\mathrm{MnCl_2{\cdot}4H_2O}$ (0.20 g, 1.0 mmol) and NaOBz (0.42 g, 3.0 mmol) in a mixture of toluene and MeCN (1:1) gave an unsymmetric dimanganese(II) complex $[\mathrm{Mn\{HB(3,5\text{-}Pr^i_2pz)_3\}(\mu\text{-}OBz)_3Mn(3,5\text{-}Pr^i_2pzH)_2}]$ **1**‡ in *ca.* 65% yield. The existence of the protonated form of the pyrazole in **1** is evident from the strong IR band observed at 3290 cm^{-1} which is assigned to the ν(NH). Complex **1** is reasonably air-stable even in solution. The molecular structure of **1**·MeCN was

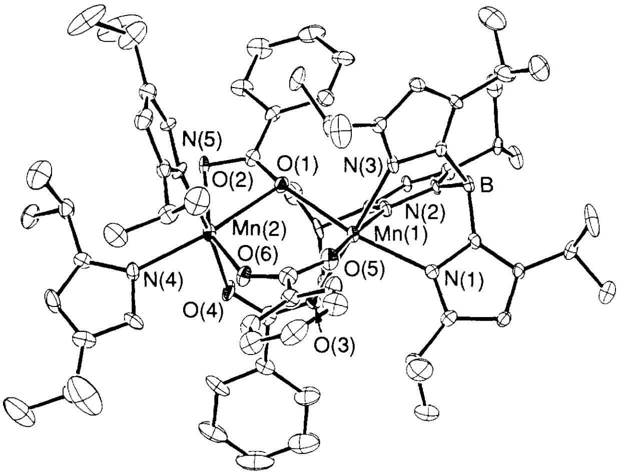

Fig. 1 ORTEP drawing of $[\mathrm{Mn^{II}\{HB(3,5\text{-}Pr^i_2pz)_3\}(\mu\text{-}OBz)_3Mn^{II}(3,5\text{-}Pr^i_2pzH)_2)}]$ **1**·MeCN. The solvent of crystallization is omitted for clarity. Selected bond distances (Å) and angles (°): Mn(1)–N(1) 2.259(8), Mn(1)–N(2) 2.281(7), Mn(1)–N(3) 2.243(3), Mn(1)–O(1) 2.264(8), Mn(1)–O(3) 2.138(4), Mn(1)–O(5) 2.201(6), Mn(2)–N(4) 2.223(8), Mn(2)–N(5) 2.304(7), Mn(2)–O(1) 2.349(6), Mn(2)–O(2) 2.235(6), Mn(2)–O(4) 2.139(5), Mn(2)–O(6) 2.095(7), Mn(1)–Mn(2) 3.753(2), Mn(1)–O(1)–Mn(2) 114.6(3), O(1)–Mn(1)–N(3) 87.8(3), N(3)–Mn(1)–O(5) 90.5(2), N(1)–Mn(1)–O(5) 92.9(3), N(4)–Mn(2)–N(5) 88.0(3), N(5)–Mn(2)–O(2) 81.0(2), N(5)–Mn(2)–O(6) 93.0(2).

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† *Abbreviations used*: $\mathrm{HB(3,5\text{-}Pr^i_2pz)_3}$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate,[12] 3,5-$\mathrm{Pr^i_2pzH}$ = 3,5-diisopropylpyrazole, OBz = benzoate, bipy = 2,2′-bipyridine.

‡ Satisfactory C, H and N analyses were obtained. IR ν/cm^{-1} (KBr): (NH) 3290, (BH) 2536, ($\mathrm{CO_2}$) 1580, 1458. FD-MS (*m/z*): 1244. μ_{eff}: 8.14 μ_{B} mol^{-1} at 295 K.

determined by X-ray crystallography§ and its ORTEP view is shown in Fig. 1.

Both manganese(II) ions are in an octahedral environment. Mn(1) is coordinated by three nitrogens from the tris(pyrazolyl)borate ligand, whereas Mn(2) is coordinated by two nitrogens from the pyrazoles. The two manganese(II) ions are bridged with three benzoate groups, forming the dinuclear complex as a neutral one. Two of the μ-benzoate groups are symmetrically bridging, whereas the other one adopts a unique coordination mode; only one oxygen from the carboxylate serves as a bridging ligand, while the other one binds to Mn(2) terminally. A structurally similar $(\mu\text{-carboxylato})_3$ unit has been found in a linear trinuclear manganese(II) carboxylato complex.[10a] The Mn–Mn separation found in **1** [3.753(2) Å] is comparable to (μ-aqua)bis(μ-carboxylato)dimanganese(II) complexes [3.739(2),[9a] 3.621(2)[9b] and 3.5950(9)[9b] Å] rather than a symmetric tris(μ-carboxylato) complex[8] [4.034(2) Å]. Clearly, the short metal–metal distance of **1** reflects the unusual $\text{tris}(\mu\text{-carboxylato})_3$ unit in which only one oxygen atom from a carboxylate group is available as a bridging ligand. The magnetic susceptibility of the powdered sample of **1** is 8.14 μ_B mol^{-1} at 295 K, indicative of a weak antiferromagnetic property.

The reaction of **1** with another bidentate nitrogen donor ligand, 2,2′-bipyridine, gave $[\mathrm{Mn\{HB(3,5\text{-}Pr^i_2pz)_3\}(\mu\text{-}OBz)_3Mn(bipy)}]$ **2**,¶ almost quantitatively, while the reaction of **1** or **2** with 1 equiv. of NaOH (powder) in MeCN to replace one μ-benzoate with μ-hydroxide gave only a mononuclear manganese(II) complex $[\mathrm{Mn\{HB(3,5\text{-}Pr^i_2pz)_3\}(OBz)(3,5\text{-}Pr^i_2pzH)}]$.[11]

We thank Professor Y. Fukuda of Ochanomizu University for the magnetic susceptibility measurement. The present research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (04225107).

Received, 21st October 1992; Com. 2/05633J

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§ *Crystal data* for **1**·MeCN, M_r 1284.26; **1**·MeCN crystallized in the triclinic space group $P\bar{1}$ with a = 13.964(3), b = 24.145(6), c = 12.478(3) Å, α = 100.29(2), β = 119.54(1), γ = 90,85(2)°, V = 3573(2) Å^3, Z = 2, D_c = 1.19 g cm^{-3}. Data collection (2° < 2θ < 45°) was completed at −85 °C to prevent the loss of MeCN molecule of crystallization. The structure was solved by the direct method (MITHRIL), and refined by the block-diagonal least-squares technique by TEXSAN. The final $R(R_w)$ value was 6.81(3.87)% for 4397 reflections ($F_o \geq 3\sigma F_o$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

¶ Satisfactory C, H and N analyses were obtained. IR ν/cm^{-1} (KBr): (BH) 2533, (CO_2) 1568, 1450. FD-MS (m/z): 1095.

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