Higher Valent Manganese Chemistry. [Mn(biguanide)₃]+, a Structurally Characterized Mn^{IV} Complex with All-nitrogen Coordination

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Oxidation of Mn^{II} acetate with Bu$^n_4$NMnO$_4$ in the presence of biguanide (big H) affords the red [Mn^{IV}(big)₃]+ cation, a rare non-porphyrinic example of a Mn^{IV} complex coordinated solely through N atoms.

Photosystem II (PS II) is thought to oxidize water to oxygen by means of a polynuclear Mn complex cycling between the 2+ and 4+ oxidation states in one-electron steps. EPR evidence led Hansson *et al.*[1] to propose a model that involves a trinuclear Mn complex adjacent to a mononuclear Mn^{IV} one. Few mononuclear Mn^{IV} complexes have been isolated, however, and fewer still structurally characterized.[2] EPR spectra of Mn^{IV} complexes containing O$_6$ and N$_2$O$_4$ coordination spheres have recently been compared with that of the oxygen-evolving centre.[3] Recent evidence supports the possibility of nitrogen coordination to Mn in PS II.[4] We report here the synthesis and characterization of [Mn(big)₃]+ (big = biguanide), a rare example (excluding porphyrins) of a structurally characterized Mn^{IV}N$_6$ complex.[5]

Air oxidation of alkaline aqueous solutions containing Mn^{II} and the ligand gives complexes[6,7] for which spectral and magnetic data indicate an antiferromagnetically coupled di-µ-oxo bridged dimeric structure.[8] By contrast, non-aqueous oxidation with Bu$^n_4$NMnO$_4$[9,10] affords the previously unreported mononuclear Mn^{IV} tris complex, [Mn(big)₃]+, as a red solid that decomposes in water, but that dissolves in Me$_2$SO and MeOH, from which it crystallizes readily.†

Structural, IR and magnetic evidence all indicate that [Mn(big)₃]OAc·2H$_2$O contains Mn^{IV} bound to three deprotonated biguanide ligands. Structurally the complex comprises of an octahedral MnN$_6$ coordination sphere with Mn–N(av.) = 1.93 Å.‡ Such Mn–N distances are short even for Mn^{IV}–N bonds (usual range from 1.955 to 2.052 Å; but see ref. 12), and effectively exclude any higher oxidation state (Fig. 1). Their shortness reflects the high affinity of Mn^{IV} for the strongly σ- and π-donating biguanide ligand. In general, bond lengths to

Mn^{IV}, like Mn$^{IV/III}$ redox potentials,[2] parallel the Lewis basicity of the ligand.

Ligand metrical features also support the formulation of a Mn^{IV} complex of deprotonated biguanide. In protonated (*i.e.* [M(bigH)]) complexes C–N distances increase in order C–N(ligand) < C–N(terminal) < C–N(ring); in [Mn(big)₃]+, however, as in [Cr(big)₃],[13] terminal bonds are shorter than those to the ring N atom. Similarly, the C–N(ring)–C angle (119°) matches that in [Cr(big)₃][13] more closely than that in [Cr(bigH)₃]³+ (127°).[14] Further evidence for deprotonation comes from IR spectroscopy. NH deformation bands at 1673 cm⁻¹ in [Cr(bigH)₃]³+ shift to 1630 cm⁻¹ in [Cr(big)₃];[15] the analogous bands occur at 1645 cm⁻¹ in [Mn(big)₃]+. Furthermore, no hydrogen atoms were found on the ring N atoms, although all other H atoms were located in the structure.

Solution magnetic moments (in Me$_2$SO) by the NMR method [µ$_{eff}$ (311 K) 3.78 µ$_B$] also establish [Mn(big)₃]+ as a *bona fide* Mn^{IV} complex. Strong (ε ≃ 6000) ligand-to-metal charge-transfer bands in [Mn(big)₃]+ [λ$_{max}$ 337, 399 and 460 (sh) nm] reversibly shift slightly, without qualitative change in the appearance of the spectrum, on addition of toluenesulfonic acid. As in the analogous M^{III} (M = Cr, Co) com-

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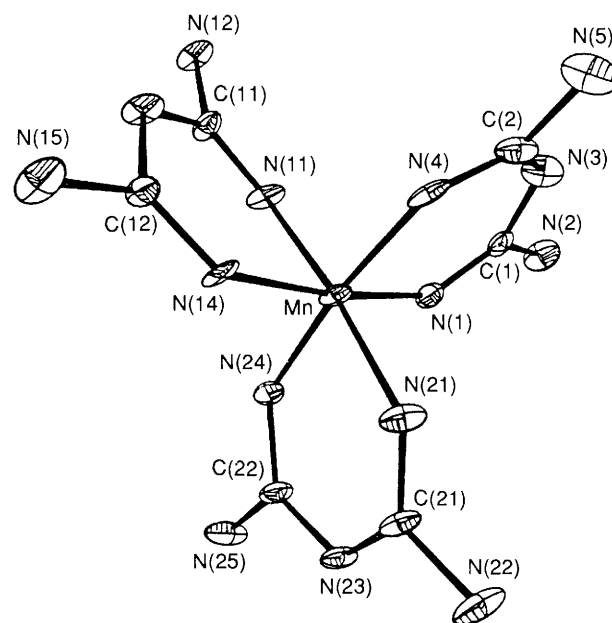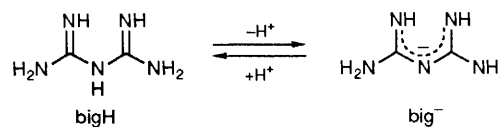† *Typical procedure* for [Mn(big)₃]OAc·2 H$_2$O: to a solution of biguanide[11] (4.0 g, 40 mmol) and Mn(OAc)$_2$·4H$_2$O (1.84 g, 7.4 mmol) dissolved in 200 ml EtOH was added with stirring Bu$^n_4$NMnO$_4$[9] (1.77 g, 4.93 mmol) for 15 min to produce a deep-red solution that deposited a red powder overnight. (*CAUTION*! Quaternary ammonium salts of permanganate have been reported to be explosive.) Addition of Et$_2$O to a filtered concentrated solution of the crude product in MeOH precipitated a red powder that was washed with Et$_2$O and dried *in vacuo*. Yield 3.31 g, 82%. Slow evaporation of a saturated methanolic solution afforded plates suitable for diffraction measurements. Analysis calc. for [Mn(big)₃]OAc·2H$_2$O (found): C 21.3 (21.9), H 5.6 (5.3), N 46.6 (46.3), Mn 12.2 (12.4). UV (Me$_2$SO), λ/nm (ε/dm³ mol⁻¹ cm⁻¹); 337 (5 900), 399 (6 100). µ$_{eff}$ (311 K) 3.78 µ$_B$.

‡ *Crystal structure data*: C$_8$H$_{25}$N$_{15}$O$_4$Mn, orthorhombic, space group *Pbca* (from MeOH), *a* = 12.931(4), *b* = 15.243(5), *c* = 19.327(5) Å, *V* = 3809(2) Å³, *Z* = 8, *D$_c$* = 1.577 g cm⁻³, *D$_o$* = 1.56 g cm⁻³. Enraf-Nonius CAD-4F diffractometer generating Mo-Kα radiation (graphite monochromator) was used at room temperature. 3856 reflections were collected, of which 1370 unique data (corrected for absorption, Lorentz, and polarization effects and with averaging of equivalent reflections) with w/F^2 > 3σ(F^2) were used in refinement. The structure was solved by Patterson methods, and the hydrogen atoms were located in the Fourier difference maps but not refined. Least-squares refinement converged to final agreement factors of *R* = 6.98% and *R$_w$* = 7.00% for 253 variables. 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.

bigH ⇌ big⁻ (–H⁺ / +H⁺)

Fig. 1 Selected bond lengths (Å) and angles (°) for [Mn(big)₃]-OAc·2H$_2$O: Mn–N(1) 1.92(1), Mn–N(4) 1.92(1), Mn–N(11) 1.948(8), Mn–N(14) 1.935(9), Mn–N(21) 1.958(9), Mn–N(24) 1.92(1); N(1)–Mn–N(4) 85.6(4), N(11)–Mn–N(14) 84.3(4), N(21)–Mn–N(24) 86.5(4), C(1)–N(3)–C(2) 118(1), C(11)–N(13)–C(12) 118(1), C(21)–N(23)–C(22) 121(1)

plexes,[15] these observations are consistent with successive protonation of the complexing ligands, rather than change in redox state or gross structure. Initial cyclic voltammetric scans of unprotonated tris-biguanide (0.1 mol dm^{-3} NEt$_4$BF$_4$ in Me$_2$SO, Pt electrode) show an irreversible reduction at -735 mV $vs.$ SCE (SCE = saturated calomel electrode). This low Mn$^{IV/III}$ potential shows the considerable stabilization of Mn^{IV} with respect to reduction by biguanide coordination.

In summary, the present results provide a benchmark for the molecular and electronic structural features associated with the MnN$_6$ core. They also show that deprotonated biguanide (and by extension guanidine) strongly stabilizes Mn^{IV} with respect to Mn^{II}.

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