Synthesis and structure of the [Mn^{IV}(biguanide)$_3$]$^{4+}$ ion: the simplest source for water-stable manganese(IV)

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Aqueous oxidation of alkaline biguanide sulfate with KMnO$_4$ followed by crystallisation from 2 M HNO$_3$ yields the mononuclear [Mn(bigH)$_3$]$^{4+}$ ion, which has been characterised crystallographically and provides an easy route to mononuclear, water-stable manganese(IV).

In aqueous solution, some oxo-bridged multinuclear manganese(IV) complexes are known to be stable enough for successful study of their solution chemistry.[1] In contrast, none of the limited number of well characterised mononuclear complexes of manganese(IV) have been synthesised from aqueous media or have been reported to be stable in aqueous solution. This situation has considerably limited our knowledge of the aqueous chemistry of manganese(IV), a key species in photosystem II. We report here the synthesis and structural characterisation of a mononuclear complex of manganese(IV) with the ligand biguanide, NH$_2$C(=NH)NHC(=NH)NH$_2$, (bigH). The crystals grow from 2 M nitric acid and are stable in aqueous solution over a wide range of acidity (10^{-6} to 2 M).

X-Ray structural studies[2] indicate that the complex ion [Mn(bigH)$_3$]$^{4+}$ contains Mn^{IV} bound to three biguanide ligands (Fig. 1). Structurally the complex comprises of an axially distorted octahedral MnN$_6$ coordination sphere with axial Mn–N(av.) 1.98 Å and equatorial Mn–N(av.) 1.917 Å. Such Mn–N distances (usual range 1.955–2.052 Å for other Mn^{IV}–N bonds[3])

effectively establish the Mn^{IV} state. The lattice consists of two types of metrically similar but crystallographically distinct [Mn(bigH)$_3$]$^{4+}$ units with sulfate and nitrate counter anions along with three molecules of water of crystallization. The two monomeric units are held together by hydrogen bonds via the sulfato anion, the latter acting as a bridge between the two. The non-bonded N···N interactions are responsible for packing in the structure (Fig. 2) with an average N···N distance of 2.414 Å. There are no significant covalent bonding contacts between the two molecules. An ORTEP[4] drawing of the complex cation with atom numbering scheme is shown in Fig. 1. The average cis and trans angles at the metal center are 89.548 and 175.085°, respectively. The four nitrogen atoms N(7), N(8), N(15) and N(21) form the equatorial plane and N(1) and N(14) are in axial positions. The Mn atom lies 0.045 Å towards the N(1) atom from the least-squares plane consisting of N(7), N(8), N(15) and N(21) atoms.

The complex was prepared by a very simple procedure. A solution of KMnO$_4$ (0.158 g, 1.0 mmol in 5 ml water) was added dropwise with stirring to 30 ml of a stirred, ice-cold aqueous solution of bigH·H$_2$SO$_4$ (1.0 g, 5.0 mmol) in NaOH (0.6 g, 15.0 mmol). The resulting deep orange–red solution was nearly neutralised by slow addition of 2–3 mL, 2 M HNO$_3$ and filtered. The filtrate was acidified to ca. 2 M by adding ca. 7.5 mL, 12 M HNO$_3$ and stored overnight at 4 °C. Red crystals suitable for diffraction measurements were collected by filtration. Yield, 0.18 g, (60% based on MnO$_4^-$). Anal.: calc. (found) for [Mn(bigH)$_3$]$_2$SO$_4$(NO$_3$)$_6$·3H$_2$O: C, 11.63 (11.3); H 3.88 (3.9); N, 40.71 (39.9)%. UV–VIS (H$_2$O, pH 2), λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 352 (8942), 430 (8035). Prominant molecular ion peaks (Kratos PC-Kompact MALDI 4 V1.0.3) found at 694.8 {[Mn(bigH)$_3$]SO$_4$(NO$_3$)$_3$·3H$_2$O}$^-$, 585.9 {[Mn(bigH)$_3$]SO$_4$-(NO$_3$)·4H$_2$O}$^+$, 101.7 {bigH$_2$}$^+$, 60 {NO$_3^-$}.

The mononuclear structure of the complex appeared somewhat surprising because of the demonstrated tendency of higher-valent manganese complexes for aquation, decomposition and polynucleation in aqueous acids.[2a] It is probably the exceptionally strong basicity of biguanide[5] which discourages the formation of multinuclear oxo-bridged manganese complexes. Hart et al.[3] isolated the complex [Mn^{IV}(big)$_3$]-

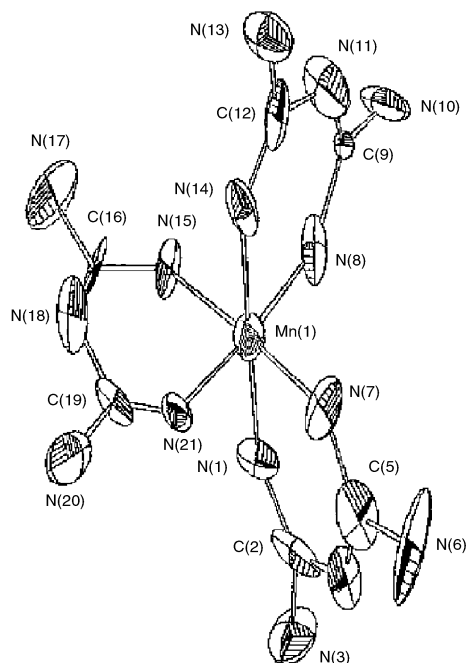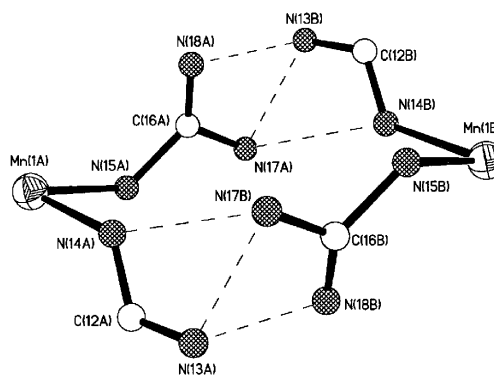**Fig. 1** ORTEP plot and labeling for [Mn(bigH)$_3$]$^{4+}$. For clarity the hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (°): Mn(1)–N(1) 1.97(2), Mn(1)–N(7) 1.91(1), Mn(1)–N(8) 1.93(1), Mn(1)–N(14) 1.99(2), Mn(1)–N(15) 1.92(1), Mn(1)–N(21) 1.91(1); N(1)–Mn(1)–N(7) 92.57(6), N(8)–Mn(1)–N(14), 86.22(4), N(15)–Mn(1)–N(21) 84.83(7).

Fig. 2 Non–bonded N···N interactions responsible for packing in the structure.
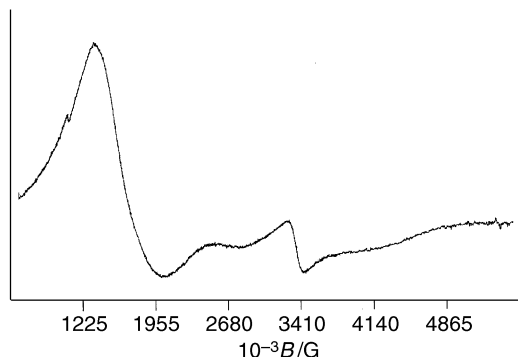
Fig. 3 X-Band EPR spectrum of polycrystalline $[Mn(bigH)_3]^{4+}$ at room temperature.

more intense and slightly asymmetric with turnover and crossover points at 1550 G (g = 4.3) and 1860 G (g = 3.58). The EPR spectrum fully corresponds to a Mn^{IV} (d^3) ion in octahedral field with axial distortion[8] consistent with the crystal structure. The MnN_6 core in $[Mn(big)_3]^+$ by contrast, is almost undistorted.[3]

The synthesis described here opens an easy route to aqueous stable Mn^{IV} which may be useful for better understanding of the aqueous chemistry of Mn in its +4 state. Presently, the kinetics of $[Mn^{IV}(bigH)_3]^{4+}$ with simple reducing agents in acidic solution are under investigation.

(OAc)·2H$_2$O by the non-aqueous oxidation of Mn^{II} acetate with $NBu^n_4MnO_4$ in the presence of bigH in ethanol. They reported no aqueous chemistry for this complex but we found that in water it forms a turbid solution the turbidity of which increased rapidly and a brown precipitate deposited slowly. This is consistent with our earlier kinetic observation[6a] that $[Ag^{III}(bigH)_2]^{3+}$ but not its conjugate base, $[Ag^{III}(big)(bigH)]^{2+}$ survives for an extended period in aqueous solution. An analogous situation was found with $[Ag^{III}\{C_2H_4(bigH)_2\}]$,[6b] $\{[C_2H_4(bigH)_2]$ is tetradentate ethylenebis(biguanide)$\}$. The electron-rich, deprotonated ligands big$^-$ and $[C_2H_4(big)(bigH)]^-$ significantly lower the kinetic barrier to intramolecular redox decomposition forming Ag$^+$ and oxidation products of the biguanide. Expectedly, a similar redox decomposition is favoured for $[Mn(big)_3]^+$ but not $[Mn(bigH)_3]^{4+}$ in solution in spite of the greater ligand field strength of big$^-$, as indicated by the fact that both the UV–VIS spectral bands of $[Mn(big)_3]^+$ appear at lower wavelengths than those of $[Mn(bigH)_3]^{4+}$.

The synthetic procedure used for $[Mn(bigH)_3]^{4+}$ failed to produce a stable $[C_2H_4(bigH)_2]$ analogue. The isolated red crystals in this case changed to a nearly colourless solid within hours. The strong-field tetradentate ligand, ethylenebis(biguanide), prefers square-planar coordination and may not be compatible with a d^3 Mn^{IV} system which prefers octahedral geometry. Notably, a square-planar Mn^{III} complex of $[C_2H_4(bigH)_2]$ has been structurally characterised.[7]

In the polycrystalline form **1** exhibits a corrected room-temperature (19 °C) magnetic moment of 3.73 μ_B consistent with a d^3 octahedral complex. Its polycrystalline X-band EPR spetrum (Fig. 3) displays broad resonances at g values (DPPH, g = 2.0037) of *ca.* 2 and 4. The signal at lower field is much

Notes and references

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2 *Crystal data* for $[Mn(bigH)_3]_2SO_4(NO_3)_6 \cdot 3H_2O$; M = 1238.0, monoclinic, space group *Ia*, a = 17.2338(17), b = 15.8698(16), c = 18.3355(18) Å, β = 103.07(1)°, U = 4884.772(46) Å^3, T = 298(1) K, Z = 4, μ(Mo-Kα) = 0.66 mm^{-1}. D_c = 1.6359 Mg m^{-3}. Data were collected (for a crystal of dimensions $0.18 \times 0.21 \times 0.19$ mm) on an Enraf-Nonius CAD4-mach 2 diffractometer and were corrected for Lorentz polarization and decay. The structure was solved by direct methods and refined on *F* using the full-matrix least squares technique using the XTAL 3.2 program package. The final R, R_w indices were 0.098 and 0.108 and goodness of fit on F^2 was 6.294. Attempts were made to solve the structure in the space group *C2/c* but a few atoms including the nitrogen and oxygen of the nitrate anion and water molecules could not be properly located. In addition, a few nitrogen atoms of the chelate ring were also unreliable owing to their high anisotropic thermal parameters leading to high residual electron density which could not be accounted for. CCDC 182/1886. See http://www.rsc.org/suppdata/cc/b0/b007013k/ for crystallographic files in .cif format.

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