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Observation of a Manganese(IV) Transient Following Oxidation of the *trans*-Dichloro(*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) Manganese(III) Ion with Hydroxyl Radical

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Examples of complexes of manganese with multidentate amine ligands in oxidation states above II are few. However, the saturated macromonocyclic tetraamines cyclam (1,4,8,11-tetraazacyclotetradecane) and its hexamethyl substituents tet*a* and tet*b* are known to form stable and apparently octahedral manganese(III) complexes [1, 2]. The manganese(IV) oxidation state is dominated by MnO_2, although recently an oxomanganese(IV) cluster incorporating the tridentate macrocyclic amine 1,4,7-triazacyclononane (tacn) with an adamantane-like geometry was characterized [3]. Several reports of transient manganese(IV) species have appeared, but none with saturated amine donor ligands [4, 5]; stable manganese(IV) complexes are usually polymeric [3, 6]. The d^3 electronic configuration is inherently inert, and we were interested in seeking information about the stability of complexed manganese(IV) monomers with this configuration. To this end, we have synthesised and characterized by an X-ray crystal structure determination the manganese(III) complex cation $Mn(teta)Cl_2^+$ (tet*a* = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), and investigated the oxidation of this cation to manganese(IV) with OH radicals generated by pulse radiolysis in neutral aqueous solution.

Chemical oxidation of a solution of $Mn(OSO_2CF_3)_2$ and tet*a* in methanol, followed by addition of concentrated HCl and cooling yields *trans*-$[Mn(teta)Cl_2]Cl$. The green complex is stable in acidic and neutral aqueous solution, and single crystals were grown from aqueous acid. The molecule ($C_{16}H_{42}Cl_3MnN_4O_3$, form. wt. 499.8) crystallized in the monoclinic space group $P2_1/c$, $a = 8.4006(8)$, $b = 12.465(2)$, $c = 11.659(2)$ Å, $\beta = 103.20(1)°$, $U = 1188.6$ Å^3, $D_x = 1.396$ g cm^{-3}, $Z = 2$, μ(Mo-Kα) = 8.44 cm^{-1}, λ(Mo Kα) = 0.71069 Å. Measurement was made on a CAD4 diffractometer, and refined to $R = 0.033$ and $R_w = 0.047$. An ORTEP drawing of the molecular cation appears in Fig. 1.

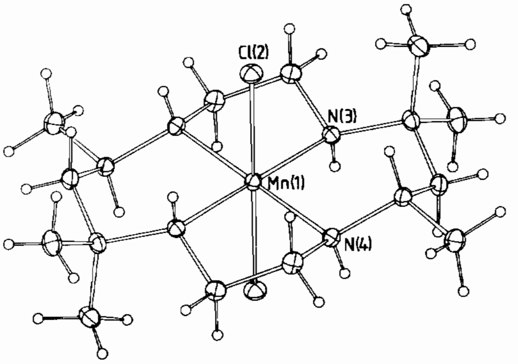

Fig. 1. ORTEP drawing of the $Mn(teta)Cl_2^+$ molecular cation; 20% thermal ellipsoids and atom labelling are shown. The centrosymmetric nature of the cation is clearly seen. Bond lengths and angles about the manganese(III) ion are: Mn–N(3) = 2.074(2), Mn–N(4) = 2.043(2), Mn–Cl(2) = 2.549(1) Å; N(3)–Mn–Cl(2) = 84.2(1), N(4)–Mn–Cl(2) = 92.0(1), N(4)–Mn–N(3) = 85.7(1), N(3)–Mn–N(3′) = 94.3(1)°.

The geometry about the manganese(III) was defined as close to octahedral. The chloride ligands are in *trans* axial sites, and the metal ion lies at a centre of symmetry (Fig. 1). There are few structurally characterized Mn(III) complexes, and none reported with saturated amine macrocycles. The Mn(III)–N bond lengths observed here (av. 2.06 Å) are significantly shorter than those in $Mn(edta)^-$ (av. 2.20 Å) [7] and longer than those in the equatorially coordinated porphyrin [Mn($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)(pyridine)Cl] (av. 2.02 Å) [8].

For *trans*-$[Mn(teta)Cl_2]^+$, a quasireversible Mn(III)/(II) couple is observed in neutral aqueous solution near +0.2 V (*vs.* Ag/Ag$^+$), but no Mn(III)/(IV) couple is observed before the solvent limit (~ +1 V). However, the powerful oxidant OH ($E°$ ~ +2 V), generated radiolytically, causes an oxidation reaction. The 1 MeV pulse radiolysis facility, optical system, and process of kinetic analysis have been described elsewhere [9]. The system was calibrated by thiocyanate dosimetry. Optical density changes were measured at 5–20 nm intervals from signal-averaged data over the range 250–600 nm, allowing construction of the intermediate absorption spectrum (Fig. 2). Kinetics of decay were followed at several

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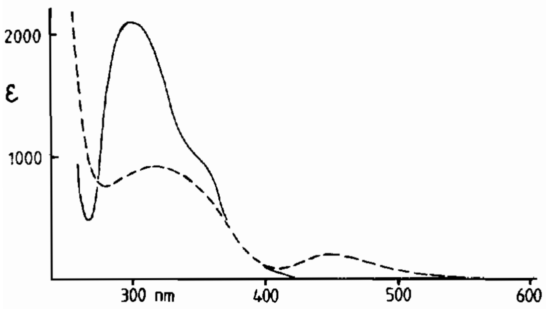

Fig. 2. Electronic spectra of the manganese(III) precursor complex (———) and the transient intermediate (– – –) from reaction of Mn(tet*a*)Cl_2^+ with OH.

wavelengths in the UV-Vis. region. Complex (mM concentration) in N_2O-saturated triply distilled water (to scavange e_{aq}^-) reacted rapidly with OH radical to yield a transient with a half-life of <1 ms which decayed by a first order process to a long-lived product.

The final optical density change indicates total consumption of the manganese(III) complex and formation of a species which absorbs light fairly uniformly across the visible region. This latter effect is consistent with the formation of suspended manganese(IV) dioxide or some close insoluble analogue, which can be detected visually in continuous pulse experiments, and is the likely final decay product in aqueous solution from a manganese(IV) transient complex. The transient spectrum has maxima at 450 nm (ϵ 190 M^{-1} cm^{-1}) and 320 nm (ϵ 920), consistent with oxidation of the manganese(III) centre to manganese(IV). The spectrum is qualitatively similar to those of first row inert d^3 chromium(III), and is also similar to that of the transient d^3 Re(IV) amine complex recently observed [10]. The spectrum is not inconsistent with those observed for other Mn(IV) transients with mainly O-donors; for example, absorbances were observed near 460 nm and 310 nm in permanganate oxidations of uracils, assigned to a manganese(IV) intermediate [4]. The stable cluster complex $[Mn_4(tacn)_4O_6]^{4+}$, where each Mn(IV) lies at a distorted octahedron of N_3O_3 donors [3], exhibits maxima at 552 nm ($\epsilon \sim 650$ per Mn centre) and 336 nm ($\epsilon \sim 4000$), somewhat similar to the transient observed here. Given both that the Mn(III) precursor is, and the expectation that d^3 Mn(IV) will be, relatively inert, oxidation to the observed transient is not expected to occur with concomitant complete ligand loss, so an octahedral monomeric manganese(IV) ion retaining essentially its initial donor set is predicted. The observed first order decay of the transient ($k_{obs} = 5.0 \times 10^3$ s^{-1}) presumably involves rate determining ligand dissociation, with the eventual product being manganese dioxide. We are currently extending our investigations to other related complexes.

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