Table I. ^1H NMR Spectral Parameters for $[Pt(N,N,N',N'\text{-}Me_4en)(Guo)_2]^{2+}$, 0.05 M in D_2O

	Chemical Shifts[a]			
T(°C)	H(8)	H(1')	NCH_3	NCH_3
100.3	8.458	5.934 5.902	2.968	2.756
90.1	8.458	5.927 5.892	2.960	2.746
64.7	8.489	5.944 5.911	2.977	2.758
48.0	8.524 8.519	5.962 5.930	2.997	2.775
38.8	8.533 8.527	5.965 5.929	3.001	2.774
26.	8.551 8.539	5.972 5.931	3.007	2.775
0.	8.607 8.583	5.990 5.950	3.039	2.800

[a] Ppm downfield from DSS.

of base-stacking interactions between complexes. As a result of the temperature dependence of the chemical shifts, the two H(8) peaks merge at ~55 °C. However the splitting of the H(1′) peaks is larger and the H(1′) chemical shifts are less dependent on temperature so that two H(1′) doublets remain at 100 °C, confirming slow exchange between the diastereomers at this temperature. A lower limit to $\Delta G^{\ddagger}$ for the interconversion between the diastereomers can be calculated from the chemical-shift difference between the two H(1′) resonances at 100 °C. This difference is 3.2 Hz at 100 °C so that $\Delta G^{\ddagger}$ for the interconversion is >86 KJ mol^{-1}. This value is large enough to allow the possibility of separating the diastereomers, and we are attempting to do so.

The chirality demonstrated for the platinum center of II should be a general phenomenon for square-planar complexes. It will occur whenever a pair of large, planar ligands occupy cis positions in the coordination sphere. If these ligands are large enough, steric considerations will prevent their occupying the coordination plane and they will twist above and below it as observed for I. Isomers A, B, and possibly C will result. For exchange to occur among them, the ligands must rotate about the metal bond and in the transition state the ligand plane will lie in the metal coordination plane. This work demonstrates that it is possible, by increasing the steric bulk of the ligands, to destabilize the transition state so that a substantial barrier results between the A, B, and C stereoisomers.

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Bis(tetramethylammonium) Tris(sorbitolato)manganate (IV), an EPR-Active Monomeric Complex of Manganese (IV)

Sir:

During recent investigations[1-5] of the redox chemistry for polyhydroxy complexes of manganese, we noted that certain of these ligands stabilize the +4 oxidation state as an apparent high-spin monomeric complex in aqueous alkaline solution. Previous examples of manganese(IV) species appear to be restricted to a series of di-μ-oxo bridged dimers that contain the $[Mn_2{}^{IV}O_2{}^{4+}]$ unit.[6-10] Their low magnetic moments (ca. $\leq 2.5\ \mu_B$) are consistent with considerable antiferromagnetic coupling between the manganese centers.[9] A few unstable halide and pseudohalide monomeric complexes of the type $[MnL_6]^{2-}$ ($L = F$,[11] Cl,[12] IO_3,[13] or CN[14]) have been reported, but they do not appear to exhibit appreciable distortion from octahedral symmetry and have not been fully characterized. A recent EPR study of a number of dioxygen adducts formed by manganese(II) porphyrins has been interpreted in terms of a manganese(IV)-peroxo formulation.[15] We report here the isolation and characterization of $(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3$ ($C_6H_{14}O_6$ = sorbital (D-glucitol)), which we believe to be the first authentic example of a high-spin tris(chelate) monomeric complex of manganese(IV).[16] The complex exhibits an EPR spectrum which is consistent with a ($1/2 \rightarrow -1/2$) transition of the spin quartet ground state in an axially distorted octahedral ligand field.

In the formation reaction,[16] the manganese(II)-sorbitol complex appears to reduce triplet-state dioxygen to hydrogen peroxide, with the yield dependent on the equilibrium constants K_1 and K_2.

$$[Mn_2{}^{II}(H_2O)_2(SH_4)_4]^{4-} + {}^3O_2 \overset{K_1}{\rightleftharpoons} \underset{(III_A)_2}{[Mn_2{}^{III}(OH)_2(SH_4)_4]^{4-}} + H_2O_2\ (8\%) \quad (1)$$

$$\underset{(III_A)_2}{[Mn_2{}^{III}(OH)_2(SH_4)_4]^{4-}} + {}^3O_2 + 2SH_6 \overset{K_2}{\rightleftharpoons} 2[Mn^{IV}(SH_4)_3]^{2-} + H_2O_2\ (60\%) \quad (2)$$

$$SH_6 \equiv C_6H_{14}O_6$$

The yields of hydrogen peroxide have been estimated by means of cyclic voltammetry in aqueous 0.5 M NaOH and 0.5 M sorbitol. The low yield in the (II → III) step is due to a further reaction between manganese(II) and hydrogen peroxide above pH 7.5.[1,5] Such a process yields manganese(III) and may produce ·OH by a process analogous to Fenton's reaction.[18,19] The equilibrium constant (K_2) has been estimated, from the concentration of hydrogen peroxide at 1 atm in 0.5 M NaOH and 0.5 M sorbitol, to be 3.44×10^1 mM atm^{-1} at 298 K.

The infrared spectrum of the solid complex, as a KBr disk, exhibits bands due to the O-H, C-H, and C-O stretching vibrations of sorbitol and a band at 560 cm^{-1}, which is assigned

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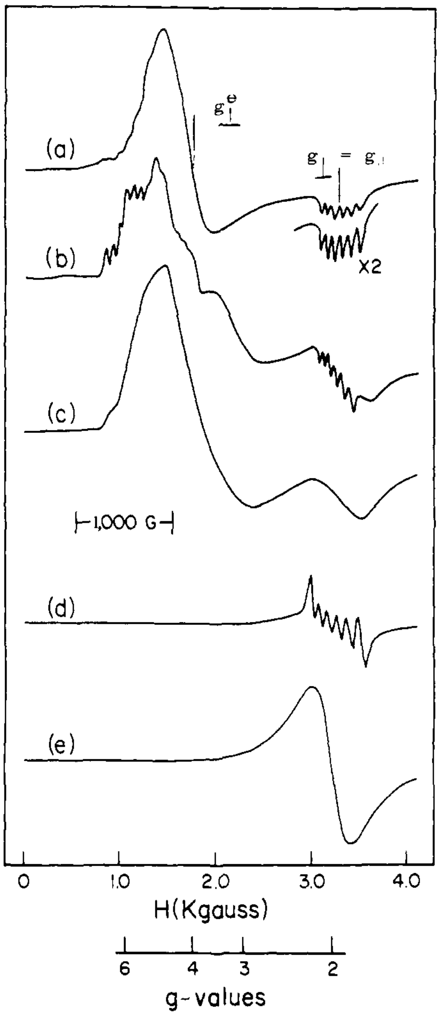


Figure 1. First derivative EPR spectra for the $(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3$ complex in various solvents: (a) aqueous 20% NaOH at 77 K; (b) methanol at 4.5 and 77 K; (c) dimethyl sulfoxide at 4.5 and 77 K or solid complex at 4.5, 77, or 298 K; (d) hexaaquo manganese(II) ion at 77 K in methanol; and (e) 0.1 M manganese(II), 0.3 M sorbitol, 0.4 M Me_4NOH in methanol at 77 K. Spectrometer settings: microwave frequency, ~9.5 GHz; modulation amplitude, 4 × 10^2, gain 4-400; scan time, 5 min, and attenuation, 5 dB.

to the Mn-O(L) stretching vibration, in agreement with similar assignments for other manganese(IV) complexes.[6-8] The absence of bands between 600 and 700 cm^{-1} confirms the absence of the $[Mn_2O_2]^{4+}$ μ-oxo bridging unit in this complex.

The results from a conductivity study in freshly prepared methanol solutions over the concentration range 0.5-2.0 mM indicate an equivalent conductance (Λ_M) of 170-210, which confirms that the complex is essentially a 2:1 electrolyte in this solvent.[20] Similar findings are obtained for dimethyl sulfoxide solutions.

Freshly prepared solutions of the complex in methanol or dimethyl sulfoxide are deep reddish orange with an intense absorption band at 265 nm, which is assigned to a ligand to metal charge-transfer transition. A shoulder at ~500 nm is assigned to a d-d transition.[1] In methanol, the ϵ values for both bands (Table I) are dependent upon the concentrations of sorbitol and hydroxide ions in the solution. This appears to be due to partial solvolysis rather than reduction to manganese(III), which is observed in aqueous media.[1] Slow reduction to a yellow-brown manganese(III) species does occur over a period of 24 h and is accelerated in the presence of UV light or elevated temperatures, and in the presence of excess ligand.[21-24]

Table I. Absorption spectral Properties for the $(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3$ Complex

conditions	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{sh}, nm	ϵ, M^{-1} cm^{-1}
(A) methanol (+Ar)	265	6 700	500	186
(B) A + 100-fold Me_4NOH	265	10 800	500	314
(C) B + 100-fold sorbitol	265	13 000	500	400
(D) dimethyl sulfoxide ($\pm O_2$, excess Me_4NOH or sorbitol)	265	10 170	500	400
(E) aqueous Mn(III) + $K_3Fe(CN)_6$ (+500-fold OH^-/sorbitol)	275	15 000	500	400

The electrochemical behavior of the polyol complexes of manganese ions in aqueous solution has been described in detail previously.[1-5] Cyclic voltammograms in dimethyl sulfoxide and dimethylformamide for the present manganese(IV)-sorbitol complex have been recorded, but these are difficult to interpret. An irreversible reduction wave at −1.3 V vs. SCE is observed in all cases and disappears upon reduction to manganese(III). Controlled potential coulometry at −1.45 V results in an apparent one-electron reduction to give a solution of manganese(III). The absorption spectrum of the resulting manganese(III) solution (Table I) is characteristic of the dimeric species $(III_A)_2$ which has a 2:1 ligand:metal stoichiometry.[1] Such a structural change during reduction in dimethyl sulfoxide may account for the irreversibility of the redox process.

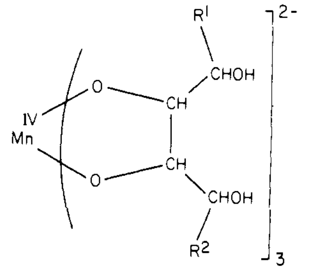
$$[Mn^{IV}(C_6H_{12}O_6)_3]^{2-} + e^- + 2H_2O \xrightarrow[E\,\sim\,-1.3\text{ V, }Me_2SO]{} \tfrac{1}{2}\underset{(III_A)_2}{[Mn_2^{III}(OH)_2(C_6H_{12}O_6)_4]^{4-}} + OH^- + C_6H_{14}O_6 \quad (3)$$

Figures 1a-c illustrate EPR spectra for the manganese(IV) complex in various solvents. The spectrum from the frozen dimethyl sulfoxide solution (Figure 1c) is identical with that obtained from a powdered sample and is almost certainly due to a precipitation of the solid complex rather than the production of a "glass". In aqueous 20% NaOH (Figure 1c), however, a clean six-line hyperfine pattern at $g = 2$ is clearly observable together with a stronger and broader resonance at $g = 4$. The spectrum from methanol (Figure 1b) apparently contains a mixture of the solid and solution species, but allows the resolution of a six-line hyperfine pattern on the broad $g = 4$ resonance. The anisotropy of the resonances is unusual for $S = 3/2$ metal ion systems. However, similar properties have been reported for several chromium(III) tris(chelates).[25] Their powder and frozen glass spectra have been interpreted[25,26] to be due to a field of axial symmetry that has a large value for the zero field splitting parameter (D) such that $D \gg h\nu$ and, hence, $g\beta H/4D \ll 1$. This assumption also implies that the transitions ($3/2 \rightarrow -3/2$) will be forbidden.

The invariance of the line width and intensity on cooling the powder from 298 to 4.5 K is in agreement with negligible population in the higher spin states (due to the large zero-field splitting). Because only transitions between the ($1/2 \rightarrow -1/2$) levels are observable, an estimate for the value of D for the frozen glass can be made:[25,26]

$$g_\perp^e \simeq 2g_\perp \left[1 - \frac{(3/16)(g_\perp \beta H)^2}{D^2}\right] \quad (4)$$

Taking the experimental values of $g_\perp^e = 3.96 \pm 0.02$ and $g_\perp = g_\parallel = 2.000 \pm 0.002$ from Figure 1a, the value of D is estimated to be (1.3 ± 0.3) cm^{-1}, which is considerably larger than the microwave quantum of 0.3 cm^{-1}. Reduction of the complex (electrochemically or with $NaBH_4$) removes the EPR signal, consistent with the production of the manganese(III) state. The



$R^1 = R^2 = CH_2OH$ (sorbitol)
$R^1 = CH_2OH$, $R^2 = CO_2H$ (D-gluconate)
$R^1 = R^2 = CO_2H$ (D-glucorate)
$R^1 = R^2 = H$ (erythritol)

Figure 2. Probable coordination geometry for tris(polyhydroxy) complexes of manganese(IV).

six-line hyperfine patterns clearly are indicative of manganese(IV) rather than manganese(II) (Figures 1d and 1e).

Addition of excess hydrogen peroxide also eliminates the EPR signal in methanol or dimethyl sulfoxide solution, and results in the evolution of dioxygen and a reduction to manganese(III) (eq 2).

The concentration of $S = 3/2$ EPR absorbing species has been estimated for the complex in dimethyl sulfoxide by use of the double integration method[27-30] (1 mM copper(II) in aqueous 10 mM EDTA was used as the integration standard). The concentration of manganese(IV) ($S = 3/2$) is ~85 ± 10% of the total manganese present.

The data are consistent with the formulation of the complex as $(Me_4N)_2Mn(C_6H_{12}O_6)_3$, a monomeric high-spin complex of manganese(IV) that exhibits an axial distortion from octahedral symmetry. This is in accord with an earlier CD study of similar complexes.[1] The large value for D, $(1.3 \pm 0.3)\ cm^{-1}$, the parameter that indicates the magnitude of the axially symmetric crystalline field, is similar to that shown by several chromium(III) tris(chelates)[25] and may also be assigned to the presence of a large dipole moment in the manganese-sorbitol bonds (Figure 2). The spectra of Figure 1 are in marked contrast to the single isotropic line centered around $g = 2$ that is observed for powdered $K_2Mn^{IV}Cl_6$ at 77 K, which is known[12] to have pure octahedral symmetry. The sorbitol is believed to chelate by its *cis*-alkoxo groups, as shown in Figure 2.

This manganese(IV) complex appears to act as a specific oxygenation (oxidation) catalyst in alkali-oxygen wood pulping.[31] Preliminary results indicate that it is capable of catalyzing both ring degradation and oxidative coupling processes in alkaline solutions of several lignin model substrates.

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$$\mathrm{Mn^{II}(ClO_4)_2 + 3C_6H_{14}O_6 + 4Me_4NOH \underset{MeOH}{\overset{O_2}{\rightleftharpoons}} [(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3]}$$
$$\mathrm{+\ 2\,Me_4NClO_4\downarrow + H_2O_2 + 24H_2O}$$

The equilibrium was driven in favor of manganese(IV) by decomposition of the hydrogen peroxide with manganese dioxide.

$$\mathrm{2H_2O_2 \xrightarrow[MnO_2/MeOH]{} 2H_2O + O_2}$$

The isolated complex contained >95% manganese(IV) on the basis of polarographic analysis and by titration with ferrous ion in aqeous 0.5 M NaOH and 0.5 M sorbitol.[1,17] An alternative method of preparation involved permanganate oxidation of manganous(II) perchlorate.

$$\mathrm{2KMnO_4 + 3Mn^{II}(ClO_4)_2 + 15C_6H_{14}O_6}$$
$$\mathrm{+\ 14Me_4NOH \xrightarrow[aqueous\ MeOH]{} 5[(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3]}$$
$$\mathrm{+\ 2KClO_4\downarrow + 4Me_4NClO_4\downarrow + 24H_2O}$$

In each case the complex was isolated as a hygroscopic red-brown powder after filtration of the reaction solution and recrystallization from methanol–ethyl acetate (1:5) and was dried (0.01 Torr) for 6–8 h (yield 93%). Microanal. Calcd for $(Me_4N)_2Mn(C_6H_{12}O_6)_3 \cdot 6H_2O$: C, 36.66; H, 8.46; N, 3.29; Mn, 6.46. Found: C, 35.90; H, 8.23; N, 3.07; Mn, 6.50. The isolated complex exhibited a room-temperature bulk magnetic moment of 4.0 ± 0.1 μ_B, in agreement with that for a high spin d^3 center (μ_{eff} 3.89 μ_B).
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Water-Soluble Complexes of Tertiary Phosphines and Rhodium(I) as Homogeneous Catalysts[1]

Sir:

The low solubility of common phosphine-transition metal complexes in water has inhibited their application to catalytic transformations in aqueous solutions. Recent experiments have established that complexes derived from $Ph_2P(m\text{-}C_6H_4\text{-}SO_3Na)$[2] are catalytically active in homogeneous olefin hydrogenation and hydroformylation reactions in water.[3-5] Complexes derived from bidentate ligands can have useful differences in chemical stability and catalytic activity from analogous complexes containing only monodentate ligands.[6] Here we report the development of coupling reactions which permit the facile conversion of (bis(2-diphenylphosphinoethyl)amine (**1**)[7,8] to a wide variety of water-soluble diphosphines

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