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High-Valent Manganese in Polyoxotungstates. 3. Dimanganese Complexes of γ-Keggin Anions[†]

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Dimanganese-substituted γ-Keggin heteropoly tungstates have been synthesized by reaction of the lacunary species γ-$[(SiO_4)W_{10}O_{32}]^{8-}$ with appropriate mixtures of Mn^{II} and MnO_4^-. The crystal structure of $[(CH_3)_3(C_6H_5)N]_4[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$ (anion **1**) was determined by X-ray diffraction. Crystallographic data: space group $P\bar{1}$, $a = 12.951(3)$ Å, $b = 14.429(3)$ Å, $c = 20.347(4)$ Å, $\alpha = 81.95(3)°$, $\beta = 88.92(3)°$, $\gamma = 67.48(3)°$, $V = 3475.2(13)$ Å^3, and $Z = 2$. The final R value is 7.29% for 15861 reflections with $I > 2\sigma(I)$. The anion has the anticipated γ-Keggin structure with virtual C_{2v} symmetry. The two Mn cations occupy adjacent, edge-shared octahedra with bridging hydroxo and terminal aqua ligands. Anion **1** can be oxidized and reduced to the corresponding $Mn^{III}Mn^{IV}$ (**2**) and Mn^{II}_2 (**3**) species respectively. The magnetic susceptibility of **1** between 2 and 300 K indicates that the Mn^{III} cations are antiferromagnetically coupled, with $J = -17.0$ cm^{-1} and $g = 1.965$. No simple magnetic behavior was observed for **2** or **3**.

Introduction

In the course of our investigations of high-valent tungstomanganates, we have examined species with one-,[1,2] three-,[3] and four[4] manganese centers. The mono- and trimanganese heteropolyanions are known to exhibit significant catalytic activity for epoxidation of alkenes.[5−11] In this paper we report the synthesis and characterization of dimanganese complexes derived from the divacant lacunary polyanion γ-$[(SiO_4)W_{10}O_{36}]^{8-}$. Comparison of the catalytic activities of the various manganese-containing polyanions will be reported elsewhere.

The redox activity of dimanganese complexes is also of interest in view of the roles such moieties play in redox-active enzymes, such as Mn catalase and ribonucleotide reductase, and in photosystem II.[12] The catalase and reductase enzymes each contain two adjacent manganese atoms bridged by oxo, hydroxo, or carboxylate ligands, and although four manganese centers are believed to be involved in the oxygen evolving protein of photosystem II, current activity is centered on a "dimer of dimers" model.

Since Hervé *et al.* reported the synthesis of the lacunary polyoxoanion γ-$[(SiO_4)W_{10}O_{36}]^{8-}$,[13] only two derivatives have been described. One is the divanadate(V)-substituted anion, γ-$[(SiO_4)W_{10}V_2O_{36}]^{6-}$, of C_{2v} symmetry, which was structurally characterized by NMR.[14] The other complex is the dichromium(III)-substituted anion in $[(n\text{-}C_4H_9)_4N]_3H_2[(SiO_4)W_{10}O_{32}\{Cr_2(OH)(CH_3CO_2)_2\text{-}(OH_2)_2\}]\cdot 3H_2O$, which has an unexpected structure in which the Cr atoms are bridged by hydroxo and two acetato ligands.[15]

Experimental Section

Tetra-*n*-butylammonium decatungstodimangano(III)silicate ($SiW_{10}Mn^{III}_2$, anion 1) was prepared starting with γ-$K_8[(SiO_4)W_{10}O_{32}]\cdot 12H_2O$ (γ-SiW_{10}) reported in the literature.[13] A solution of γ-SiW_{10} (6.0 g, 2.0 mmol) in 15 mL of deionized water was quickly adjusted to pH = 3.9 with concentrated nitric acid. The pH of this solution was kept between 3.8 and 4.5 with nitric acid while solutions A and B as described below were added. The addition of solution A [0.784 g, 3.2 mmol, of manganese(II) acetate, $Mn(OAc)_2\cdot 2H_2O$, in 10 mL of water] afforded an orange solution. After the solution had been stirred for 2 min, solution B [potassium permanganate (0.126 g, 0.8 mmol) in 10 mL of water] was added dropwise. The proportions of Mn^{II} and Mn^{VII} were chosen to yield Mn^{III}. The color of the solution changed from orange to brown. After about 5 min, addition of solid tetra-*n*-butylammonium (TBA) nitrate (3.0 g) resulted in a brown precipitate. The precipitate was filtered off and purified by twice dissolving it in CH_3CN and then adding water to reprecipitate the product. About 6 g of purified compound was obtained. Anal. Calcd for $[(C_4H_9)_4N]_4[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]\cdot 1.5CH_3CN\cdot 2H_2O$: C, 21.13; N, 2.02; H, 4.06; W, 48.33; Mn, 2.89; Si, 0.74. Found: C, 21.55; N, 1.99; H, 4.14; W, 47.57; Mn, 2.83; Si, 0.80. The manganese oxidation state(s) for all $SiW_{10}Mn_2$ salts were confirmed by coulometry.

Trimethylphenylammonium Decatungstodimangano(III)silicate. Addition of a saturated solution (10 mL) of trimethylphenylammonium

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[†] Parts 1 and 2: see refs 2 and 4, respectively.

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Table 1. Crystal Data and Structure Refinement for $(Me_3PhN)_4[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$

temp: 293(2) K
wavelength: 0.71073 Å
space group: $P\bar{1}$
unit cell dimenss
$a = 12.951(3)$ Å
$b = 14.429(3)$ Å
$c = 20.347(4)$ Å
$\alpha = 81.95(3)°$
$\beta = 88.92(3)°$
$\gamma = 67.48(3)°$
volume = 3475.2(13) $Å^3$
$Z = 2$
density (calcd): 3.000 g/cm^3
abs coeff: 16.935 mm^{-1}
$F(000)$: 2828
cryst size: 0.3 × 0.2 × 0.08 mm^3
θ range for data collcn 1.54 to 27.50°
index ranges: $-1<h<16, -17<k<18, -26<l<26$
no. of reflcns collcd: 18088
no. of indep reflcns: 15957 [R(int) = 0.0713]
refinement method: Full-matrix least-squares (F^2)
data/restraints/params: 15861/0/466
goodness-of-fit on F^2: 1.010
final R indices [$I > 2\sigma(I)$]: R1 = 0.0729, wR2 = 0.1828
R indices (all data): R1 = 0.1136, wR2 = 0.2191
largest diff peak and hole: +3.600 and −5.812 e/$Å^3$

chloride in CH_3CN to a solution of the tetra-*n*-butylammonium salt of $SiW_{10}Mn^{III}{}_2$ (2.5 g in 3 mL CH_3CN) afforded a brown precipitate. The brown solid was filtered off and redissolved in CH_3CN-H_2O (1:1 v/v). As acetonitrile was allowed to evaporate at room temperature, single crystals were formed. Yield: 30%. Anal. Calcd for $[(CH_3)_3(C_6H_5)N]_4[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$: C, 14.59; N, 2.55; H, 2.07; W, 55.87; Mn, 3.34; Si, 0.85. Found: C, 14.53; N,2.42; H, 1.96; W, 56.58; Mn, 3.18; Si, 0.73.

Tetra-*n*-butylammonium Decatungstodimangano(III,IV)silicate (Anion 2). The pH of a solution of γ-SiW_{10} (3.0 g, 1.0 mmol) in deionized water (10 mL) was quickly adjusted to 1.0 with concentrated nitric acid. Addition of solution A [0.343 g. $Mn(OAc)_2\cdot 2H_2O$ in 5.0 mL of water] produced an orange solution. After this solution had been stirred for 3 min, solution B (0.0948 g. $KMnO_4$ in 5 mL water) was added dropwise and caused a color change to brown. The pH was kept below 4 during the addition of solutions A and B, the proportions of which were chosen to yield $Mn^{III}Mn^{IV}$. The solution was continually stirred for another 2 min before the addition of tetra-*n*-butylammonium nitrate (5 g) yielded a brown precipitate which was purified as described for the TBA salt of **1** with acetonitrile and water. Anal. Calcd for $TBA_{3.5}H_{5.5}[(SiO_4)W_{10}Mn_2O_{36}]\cdot 10H_2O\cdot 0.5CH_3CN$, anion **2**: W, 50.09; Mn, 2.99; Si, 0.76; C, 18.63; N, 1.53; H, 3.47. Found: W, 50.12; Mn, 2.83; Si, 0.69; C, 19.02; N, 1.52; H, 3.31.

Potassium Decatungstodimangano(II)silicate. (Anion 3). A solution of $Mn(OAc)_2\cdot 2H_2O$ (1.6 g) in water (15 mL) was added dropwise to a solution of γ-$K_8[(SiO_4)W_{10}O_{32}]\cdot 12H_2O$ (10 g) in water (40 mL) at pH = 3.9 adjusted by acetic acid. The initial colorless solution became orange. After the solution had been stirred for 5 min, addition of solid potassium chloride (20 g) afforded about 10 g of orange precipitate upon cooling in an ice bath. The precipitate was dissolved in 15 mL of hot water and reprecipitated in an ice bath. About 5 g of final product was obtained. Anal. Calcd for $K_6[(SiO_4)W_{10}Mn_2O_{36}H_6]\cdot 23H_2O$ ($SiW_{10}Mn^{II}{}_2$): W, 56.48; Mn, 3.34; K, 7.11. Found: W, 56.09; Mn, 2.77; K, 8.39.

X-ray Diffraction. Data collection proceeded using a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Single crystals of $[(CH_3)_3(C_6H_5)N]_4[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$ grew in a H_2O-CH_3CN solution at room temperature. The data collection was carried out at room temperature. Crystal data and structure refinement parameters are listed in Table 1. The structure was solved by direct methods (SHELXL-PLUS) to yield positions of W, Mn, and Si atoms, and refined with SHELXL-93 (Sheldrick, G. M.) by full-matrix least-squares, the minimized function being $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was $w = 1/[\sigma^2(F_o{}^2) + (0.1340P)^2]$ where $P = [\mathrm{Max}\,(F_o{}^2,0) + 2F_c{}^2]/3$. The space group is $P\bar{1}$, and $Z = 2$. Tungsten, manganese, and silicon atoms were refined anisotropically. The final R value is 7.29% (11.92% before anisotropic refinement) for 15861 reflections. An absorption correction (SHELXA) was made in the final refinement. An ORTEP representation of the structure of $[SiO_4W_{10}Mn_2O_{36}]^{m-}$ is shown in Figure 1. The atomic coordinates of the anion are listed in Table 2 and selected bond lengths or bond length ranges are listed in Table 3.

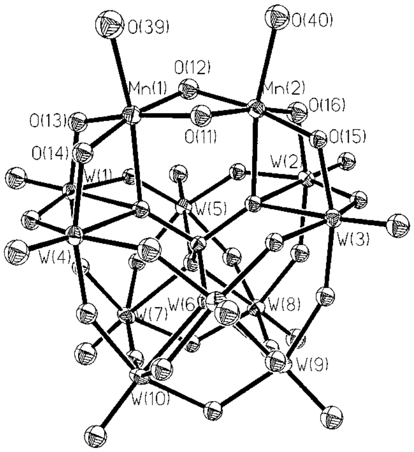

Figure 1. ORTEP view of the structure of $[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6]^{4-}$ (anion **1**), showing 50% probability ellipsoids.

Electrochemistry. Cyclic voltammograms and controlled potential electrolyses were recorded as described earlier.[2] Cyclic voltammograms for the tetra-*n*-butylammonium (TBA) salt of **1** were recorded in a 1:1 (v/v) mixture of 0.1 M $(TBA)ClO_4$ in CH_3CN and an aqueous 0.1 M potassium acetate−acetic acid buffer pH = 4.7. Controlled-potential electrolysis for the tetra-*n*-butylammonium salt was carried out in the same medium. A 0.2 M potassium acetate−acetic acid buffer, pH = 4.7, was used as the supporting electrolyte for cyclic voltammetry and controlled-potential electrolysis of the potassium salt. For cyclic voltammetry, scan rates were 40 mV s^{-1} and were initiated at the rest potential (potential of zero charge).

Magnetochemistry. Magnetic susceptibility data were recorded on polycrystalline samples of $[(CH_3)_3(C_6H_5)N]_4[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$, $TBA_{3.5}H_{5.5}[(SiO_4)W_{10}Mn^{III}Mn^{IV}O_{36}]\cdot 10H_2O\cdot 0.5CH_3CN$, and $K_6[(SiO_4)W_{10}Mn^{II}{}_2O_{36}H_6]\cdot 23H_2O$ at 2−300 K using a Quantum Design Corp. MPMS-5S SQUID susceptometer. Measurements and calibration techniques are described elsewhere.[16]

Other Measurements. Solid state IR spectra, UV/vis, near-IR, ESR, pH measurements, and elemental analysis were performed as described.[3] All chemicals were analytical grade or better and used without further purification.

Results and Discussion

Crystal Structure. There is one ordered polyanion, $[(SiO_4)W_{10}Mn_2O_{36}]^{m-}$, in each asymmetric unit. Of the five possible Baker−Figgis isomers,[17] generated by the rotation of one, two, three, or four edge-shared M_3O_{13} units of the Keggin (α) structure by 60°, only three (α-, β-, and γ-isomers) have been identified. The structure of $SiW_{10}Mn_2$ is that of a γ-isomer in which two adjacent edge-shared WO_6 octahedra have been replaced by MnO_6 octahedra. In the precursor SiW_{10} anion these octahedra are missing.

The two adjacent manganese atoms have a separation of 2.93 Å. The interatomic metal cation distances are 3.3−3.4 Å for the edge-shared WO_6 octahedra, and 3.1−3.2 Å for edge-shared W···Mn octahedra (Supporting Information).

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]^{4-}$

atom	*x*	*y*	*z*	*U*(eq)[a]
W(1)	−1739(1)	8958(1)	3217(1)	20(1)
W(2)	330(1)	5161(1)	2072(1)	18(1)
W(3)	−1136(1)	4115(1)	3039(1)	18(1)
W(4)	−3263(1)	7960(1)	4170(1)	20(1)
W(5)	−584(1)	7928(1)	1689(1)	19(1)
W(6)	−3721(1)	5722(1)	3767(1)	20(1)
W(7)	−3339(1)	9070(1)	1715(1)	21(1)
W(8)	−2157(1)	6913(1)	1050(1)	20(1)
W(9)	−3796(1)	5710(1)	2145(1)	20(1)
W(10)	−5012(1)	7882(1)	2785(1)	22(1)
Si	−2056(4)	6780(4)	2790(2)	14(1)
Mn(2)	450(2)	5043(2)	3646(1)	20(1)
Mn(1)	−597(2)	6926(2)	4223(1)	21(1)
O(40)	1924(13)	4166(12)	4303(8)	33(3)
O(39)	562(14)	6657(13)	5051(8)	42(4)
O(38)	−3234(10)	6597(9)	2838(6)	16(2)
O(37)	−2044(11)	7445(10)	2072(6)	22(3)
O(36)	−1966(10)	7412(10)	3392(6)	18(3)
O(35)	−1015(10)	5679(9)	2852(6)	17(3)
O(34)	−4407(11)	8564(10)	2105(7)	24(3)
O(33)	−3249(10)	8286(10)	1003(6)	21(3)
O(32)	−3191(11)	6387(10)	1456(7)	23(3)
O(31)	−5046(10)	6993(10)	2157(6)	21(3)
O(30)	−4345(11)	8333(10)	3437(7)	24(3)
O(29)	−2951(10)	9288(10)	2558(6)	19(3)
O(28)	−967(11)	5731(10)	1467(7)	23(3)
O(27)	−2339(10)	4729(10)	2365(6)	21(3)
O(26)	−1919(11)	9116(10)	1427(6)	21(3)
O(25)	−1046(11)	7470(10)	937(7)	25(3)
O(24)	−4177(11)	5247(10)	3012(7)	22(3)
O(23)	−5085(11)	6889(10)	3504(7)	25(3)
O(22)	−713(10)	8345(9)	2555(6)	17(3)
O(21)	252(10)	6559(10)	2010(6)	19(3)
O(20)	−2275(10)	4765(9)	3670(6)	17(3)
O(19)	−3260(12)	6566(11)	4206(7)	29(3)
O(18)	−139(10)	4040(10)	2332(6)	19(3)
O(17)	−2942(10)	9116(10)	3844(6)	21(3)
O(16)	1186(12)	4807(11)	2840(7)	28(3)
O(15)	−11(10)	3937(9)	3660(6)	17(3)
O(14)	−1933(11)	7374(10)	4705(6)	22(3)
O(13)	−691(11)	8232(10)	3904(7)	23(3)
O(12)	628(11)	6286(11)	3678(7)	26(3)
O(11)	−497(11)	5517(10)	4379(7)	25(3)
O(10)	−6362(11)	8707(11)	2746(7)	27(3)
O(9)	−4368(12)	5144(11)	1665(7)	30(3)
O(8)	−2212(12)	6654(11)	254(7)	28(3)
O(7)	−4198(13)	10234(12)	1330(8)	35(4)
O(6)	−4221(12)	5077(11)	4404(7)	28(3)
O(5)	431(11)	8314(11)	1339(7)	27(3)
O(4)	−4179(12)	8429(11)	4766(7)	31(3)
O(3)	−1131(12)	2936(11)	3162(7)	29(3)
O(2)	1316(11)	4678(10)	1522(7)	23(3)
O(1)	−1671(12)	10141(11)	3181(7)	32(3)

a: U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Four $[(CH_3)_3PhN]^+$ cations, two acetonitrile and one water molecule were located with each polyanion. The water molecule, O1W, is close enough to form hydrogen bonds with the terminal ligand, O(40), of Mn(2) and the terminal ligand, O(6), of W(6) in another anion. The O1W···O distances are listed in Table 3.

On the basis of the charge balance, six protons are associated with each $SiW_{10}Mn_2$ polyanion. These could be confidently located from bond valence sum (BVS) calculations, where

$$\mathrm{BVS} = \sum \mathrm{BV}_i = \sum \exp[(r_0 - r_i)/B]$$

and $r_0 = 1.917$ Å for $W^{6+}-O^{2-}$, $r_0 = 1.76$ Å for $Mn^{3+}-O^{2-}$, $r_0 = 1.624$ Å for $Si^{4+}-O^{2-}$, and $B = 0.37$.[18]

Table 3. Selected Bond Lengths (Å) or Bond Ranges (Å) for $[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]^{4-}$

Mn(1)−O(13)	1.863(14)	Mn(1)−O(14)	1.905(13)
Mn(1)−O(12)	1.923(14)	Mn(1)−O(11)	1.967(14)
Mn(1)−O(39)	2.17(2)	Mn(1)−O(36)	2.306(13)
Mn(2)−O(15)	1.902(13)	Mn(2)−O(16)	1.89(2)
Mn(2)−O(12)	1.90(2)	Mn(2)−O(11)	1.941(14)
Mn(2)−O(40)	2.19(2)	Mn(2)−O(35)	2.328(12)
O(1W)−O(6)	2.703	O(1W)−O(40)	2.747

W−O (terminal)	1.68(2)−1.748(14)
W−O (corner−shared)	1.879(12)−2.00(2)
W−O (edge−shared)	1.829(14)−1.959(13)
W−O (internal)	2.276(12)−2.340(14)
Si−O	1.632(13)−1.658(14)

Table 4. Bond Valence Sums (BVS) for Oxygen Atoms in $[(Me_3Ph)N]_4[(SiO_4)W_{10}Mn_2IIIO_{36}H_6]\cdot 2CH_3CN\cdot H_2O$

	oxygen	BVS	oxygen	BVS
terminal	W(1)−O(1)	1.64	W(2)−O(2)	1.85
	W(3)−O(3)	1.89	W(4)−O(4)	1.78
	W(5)−O5	1.70	W(6)−O(6)	1.58
	W(7)−O(7)	1.77	W(8)−O(8)	1.70
	W(9)−O(9)	1.80	W(10)−O(10)	1.83
	Mn(1)−O(39)	0.33	Mn(2)−O(40)	0.31
bridging	Mn(2)−O(11)−Mn(1)	1.19	Mn(2)−O(12)−Mn(1)	1.32
	Mn(1)−O(13)−W(1)	1.92	Mn(1)−O(14)−W(4)	1.87
	Mn(2)−O(15)−W3	1.83	Mn(2)−O(16)−W(2)	1.98
	W(1)−O(17)−W(4)	1.85	W(2)−O(18)−W(3)	1.98
	W(4)−O(19)−W(6)	1.92	W(3)−O(20)−W(6)	1.95
	W(2)−O(21)−W(5)	1.98	W(1)−O(22)−W(5)	1.94
	W(6)−O(23)−W(10)	1.93	W(6)−O(24)−W(9)	1.89
	W(5)−O2(5)−W(8)	2.01	W(5)−O(26)−W(7)	1.90
	W(3)−O(27)−W(9)	2.01	W(2)−O(28)−W(8)	1.98
	W(1)−O(29)−W(7)	1.96	W(4)−O(30)−W(10)	1.97
	W(9)−O(31)−W(9)	1.99	W(8)−O(32)−W(9)	2.03
	W(7)−O(33)−W(8)	1.91	W(7)−O(34)−W(10)	2.03
internal	O(35)	1.89	O(36)	1.84
	O(37)	1.95	O(38)	1.93

The bond valence sums of oxygens in the polyanion are listed in Table 4, and fall within the range 1.59−2.03 except for O(11), O(12), O(39), and O(40). The bridging atoms, O(11) and O(12), have BVS values of 1.19 and 1.32, and are therefore presumed to be hydroxo groups. The terminal oxygens [O(39) and O(40)] have much lower BVS values (0.33 and 0.31), indicating H_2O ligands. This conclusion is consistent with other manganese(III)-substituted polyanions, $[(XO_4)W_{11}O_{35}Mn^{III}OH_2]^{n-}$, which have terminal aqua ligands. The BVS values of manganese (3.2−3.3), tungsten (5.7−6.2), and silicon (3.9) fall within the expected limits.

Manganese(III) can be subject to Jahn−Teller distortion, and this can be accommodated by the Mn sites in **1**: two long axial bonds, terminal O(39) [2.17(2) Å] and O(40) [2.19(2) Å] and internal O(36) [2.306(13) Å] and O(35) [2.328(12) Å], and four relatively short equatorial bonds all ca. 1.9 Å.

The Mn···Mn distance is longer than that observed (2.676 Å) in the dimanganese(III) complex $\{[Mn^{III}_2(\mu\text{-}O)_2(BMPEA)_2](ClO_4)$, BMPEA = *N*,*N*′-bis(2,6-dimethylpyridyl)-1,2-diaminoethane} which has two oxo bridging groups[19] and is comparable to that (2.931 Å) in the triply-bridged species $\{[Mn^{III}_2(salDP)(\mu\text{-}OCH_3)(\mu\text{-}OAc)(\mu\text{-}HOCH_3)](ClO_4)\}$.[20]

Magnetochemistry. Polycrystalline $[(CH_3)_3(C_6H_5)N]_4[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$ exhibits non-Curie−Weiss behavior, and a broad maximum in the susceptibility, peaking at

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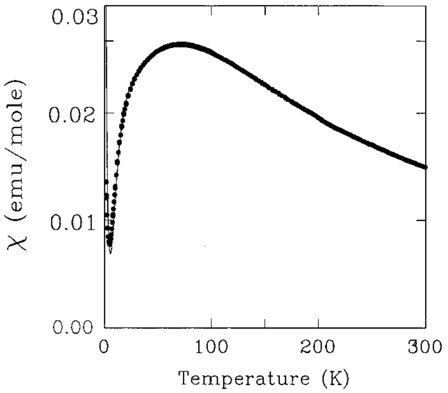

Figure 2. The magnetic susceptibility of $(Me_3PhN)_4[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$ plotted as a function of temperature. The line drawn through the data is the fit to the $S = 2$ binuclear model as described in the text.

70 K, is consistent with a moderately strong antiferromagnetic exchange. Magnetic exchange in a binuclear species can be represented by the isotropic Heisenberg spin Hamiltonian[16]

$$H = -2JS_1\cdot S_2 \tag{1}$$

where a negative J denotes a ground state singlet, and in the case of **1**, $S_1 = S_2 = 2$. The resulting magnetic susceptibility can be expressed as follows:[16]

$$\chi = \frac{2Ng^2\mu_B^2}{kT} \times \frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{28x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{28x}} \tag{2}$$

$x = J/kT$, and all other parameters have their usual meanings.

The magnetic susceptibility data were analyzed with eq 2 and the results of a least-squares fit yields parameters $g = 1.965$, $J = -17.0$ cm^{-1}, and an additional term to correct for an intermolecular coupling $zJ' = 0.391$ K.[16] The data were also corrected for 1.0% of a paramagnetic [monomeric Mn(III)] impurity. The result of this fit is illustrated in Figure 2 where the magnetic susceptibility is plotted as a function of temperature and the smooth curve is from the theoretical calculation.

Although the antiferromagnetic interaction in **1** ($J = -17.0$ cm^{-1}) is not as large as that observed in $\{Mn^{IV}_2O_2\}$ complexes such as $[Mn_2(\mu\text{-}O)_2(phen)_4]^{4+}$ ($J = -144$ cm^{-1}), or $\{Mn^{III}Mn^{IV}O_2\}$ complexes such as $[Mn_2(\mu\text{-}O)_2(phen)_4]^{3+}$ ($J = -150$ cm^{-1}),[21] it is larger than that in most dimanganese(III) complexes, such as $[Mn_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2L_2]\cdot 4CH_3CN$ [L = hydrotris(1-pyrazolyl)$_3$] with $J = -0.2$ to -0.7 cm^{-1}.[22] It is expected that the superexchange interaction is small through the $d(x^2 - y^2)$ orbital because there is no electron in this orbital based on the distortion. However, the two Mn^{III} may be close enough to interact through the $d(z^2)$, $d(xz)$, and $d(yz)$ orbitals.

No maxima were observed in the $\chi-T$ plots for salts of **2** and **3**; see Figure 3. The high temperature magnetic susceptibility data for these two polyanions were fitted to the standard Curie−Weiss equation, (3).

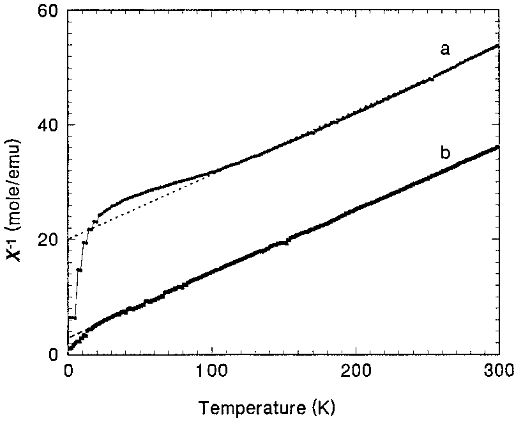

Figure 3. Inverse magnetic susceptibilities *vs* temperature: (a) $[(n\text{-}Bu)_4N]_{3.5}H_{5.5}[(SiO_4)W_{10}Mn^{III}Mn^{IV}O_{36}]\cdot 0.5CH_3CN\cdot 10H_2O$; (b) $K_6[(SiO_4)W_{10}Mn^{II}_2O_{36}H_6]\cdot 23H_2O$. The line drawn through the data is the fit to the Curie−Weiss model as described in the text.

$$\chi = \frac{C}{T - \Theta} + \text{TIP} = \frac{Ng^2\mu_B^2\{S(S+1)\}}{3k(T - \Theta)} + \text{TIP} \tag{3}$$

The results of Curie−Weiss fits are shown in Figure 3 for $TBA_{3.5}H_{5.5}[(SiO_4)W_{10}Mn^{III}Mn^{IV}O_{36}]\cdot 10H_2O\bullet 0.5CH_3CN$, where $C = 8.93$ emu·K/mol, $\Theta = -179$ K, and TIP = 0.000 emu/mol, and for $K_6[(SiO_4)W_{10}Mn^{II}_2O_{32}(HO)_2(H_2O)_2]\cdot 23H_2O$, where $C = 8.961$ emu·K/mol, $\Theta = -25.7$ K, and TIP = 0.000 emu/mol. The negative Θ values in both polyanions are consistent with antiferromagnetic exchange.

Electrochemistry. The cyclic voltammogram of the TBA salt of **1**, Figure 4a, shows an anodic peak at 720 mV and two cathodic peaks at 430 and 100 mV which indicate manganese redox processes. The two quasi reversible peaks at $E = {}^1/_2(E_{pa} + E_{pc}) = -830$ and -890 mV correspond to W^{6+} reductions. The rest potential of a solution of **1** lies between the two cathodic peaks at 430 and 100 mV, which suggests that this heteropolyanion can be reduced and oxidized.

Controlled-potential electrolytic reduction of a solution containing 0.37 g of the TBA salt of **1** in 15 mL of CH_3CN/H_2O at −200 mV resulted in the transfer of 2 equiv/mol. The color of the solution changed from brown to yellow which suggests that both manganese atoms had been reduced to Mn^{II},[1,2] i.e. formation of **3**. The cyclic voltammogram of the reduced solution (Figure 4c) is slightly different from that of **1**.

Controlled potential oxidation of **1** (0.37 g of TBA salt in 15 mL of CH_3CN/H_2O) at 1.15 V, yielded a dark brown solution and the transfer of 1.3 equiv/mol. Electrolytic reduction of the oxidized solution at −0.50 V resulted in transfer of 3 equiv. The color of the reduced solution was yellow (**3**). We therefore conclude that the oxidized product is anion **2**, which was isolated by addition of water to the oxidized solution and purified by dissolution in acetonitrile and reprecipitation with water. The cyclic voltammogram of **2**, Figure 4b, is virtually identical to that of **1**, except for the rest potential. It was not possible to oxidize this species further by electrolysis.

The TBA salt of **2** can also be obtained by direct synthesis as described in the Experimental Section. Electrolytic reduction of a solution of this salt (0.37 g in 15 mL of CH_3CN/H_2O) at −500 mV resulted in transfer of 2.9 equiv. The color of the solution changed from brown to yellow. Both salts of **2** were ESR-silent at 77 K.

Most dimanganese complexes are reported to show two separate reversible or quasi-reversible CV peaks for $Mn^{III}_2/Mn^{III}Mn^{IV}$ and $Mn^{III}Mn^{IV}/Mn^{IV}_2$.[12] Two separate quasi-reversible peaks, corresponding to Mn^{II}/Mn^{III}, Mn^{III}/Mn^{IV} and Mn^{II}_3/Mn^{III}_3,

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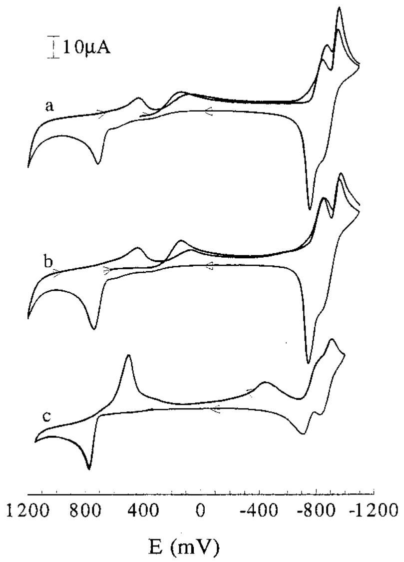

Figure 4. Cyclic voltammograms of TBA salt of 1.0 mM $SiW_{10}Mn_2$ heteropolyanions in 50% v/v CH_3CN/H_2O: (a) anion **1**; (b) anion **2**; (c) anion **3**.

$Mn^{III}{}_3/Mn^{IV}{}_3$, have also been observed in Si-centered mono- and trimanganese substituted Keggin complexes,[1,3] respectively. However, only peaks corresponding to $Mn^{III}{}_2/Mn^{II}{}_2$ and $Mn^{III}{}_2/Mn^{III}Mn^{IV}$ are observed for $SiW_{10}Mn_2$. The apparent inaccessibility of the $Mn^{IV}{}_2$ species is curious. We note that the dichromium(III) derivative, with which the $Mn^{IV}{}_2$ complex would be isoelectronic, adopts a different structure with bridging acetate groups (Cr···Cr, 3.28 Å;[15] cf. Mn···Mn in **1**, 2.935 Å)

Spectroscopy. The absorption spectra of solutions of **1**, **2**, and **3**, are shown in Figure 5. The presumed d−d band of **1** at 460 nm (1.15×10^3 L·mol^{-1}·cm^{-1}), represents a 30-nm blue-shift relative to the monomanganese(III)-substituted Keggin anion.[1,2] There is a shoulder at 550 nm (2.8×10^2 L·mol^{-1}·cm^{-1}) followed by a broad shoulder extending to the near-IR region. The latter could be the O → Mn^{III} charge transfer band, which appears at about 800 nm in the monomanganese(III)-substituted Keggin anion. The d−d transition in **2**, at *ca* 440 nm, overlaps with the O → Mn^{IV} charge transfer band. No intervalence charge transfer (IT) band is evident for **2**. It is possible that this band has moved to a shorter wavelength (as compared with the IT band of the dimanganese(III−IV) complex with 2,2′-bipyridine which occurs at 830 nm),[23] and is overlapped by the tail of the d−d band.

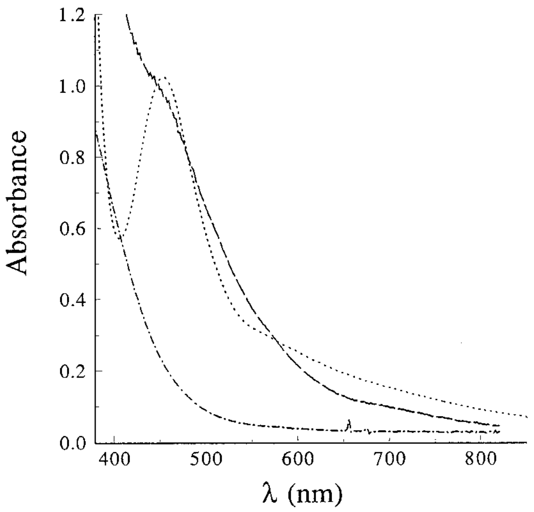

Figure 5. Absorption spectra of 1.0 mM heteropolyanion in acetonitrile: (a, · − ·) $K_6[(SiO_4)W_{10}Mn^{II}{}_2O_{36}H_6]\cdot 23H_2O$; (b, ···) $[(n\text{-}Bu)_4N]_4[(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6]\cdot 1.5CH_3CN\cdot 2H_2O$; (c—) $[(n\text{-}Bu)_4N]_{3.5}H_{5.5}[(SiO_4)W_{10}Mn^{III}Mn^{IV}O_{36}]\cdot 0.5CH_3CN\cdot 10H_2O$.

The TBA salt of **2** is not very stable in the solid state at room temperature and is partially reduced to **1** after several days.

Oxidation of 1 by Iodosylbenzene. When a solution of the TBA salt of **1** (10 g) in 20 mL acetonitrile was stirred with 6 g of $(PhIO)_n$ for 5 min, the 460-nm absorption band of **1** diminished in intensity. The excess oxidant was filtered off, and addition of water (40 mL) to the filtrate yielded a sticky dark brown material. The supernatant was poured off and the sticky species became a brown powder upon drying in air. The UV/vis and IR spectra of this product are the same as those of **2** obtained by direct synthesis or electrolysis. This compound is not very stable and is partially reduced to **1** after several days.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, interatomic distances, and selected bond lengths, a unit cell packing diagram, and a figure showing IR spectra of salts of anions **1, 2,** and **3** (8 pages). Ordering information is given on any current masthead page.

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