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Use of Tetra-*n*-butylammonium Permanganate for Inorganic Syntheses in Nonaqueous Solvents. Preparation and Structure of a Manganese(III) Dimer Containing Bridging Phenoxo Oxygen Atoms

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The use of N-*n*-Bu_4MnO_4 for the synthesis of inorganic complexes in nonaqueous solvents is explored. A reaction system leading to the preparation of known $Mn(pic)_3 \cdot H_2O$ (**1**) (picH = picolinic acid) is described. **1** can be synthesized in high yields (40–70%) by using EtOH, MeCN, DMF, and Me_2CO as solvents. With salicylic acid ($salH_2$) in pyridine (pyr) the product, after recrystallization from EtOH/petroleum spirits, is the new compound $[Mn(EtOH)_4][Mn_2(sal)_4(pyr)_2]$ (**2**). Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.142$ (3) Å, $b = 16.742$ (5) Å, $c = 10.842$ (2) Å, $\beta = 97.15$ (1)°, and $Z = 2$ at $T = -160$ °C. The anion consists of two Mn(III) atoms bridged by two μ-phenoxo oxygen atoms from salicylate groups whose carboxylates are also bound to the metal. Each Mn(III) additionally contains another salicylate and a pyridine; the dimer has C_i symmetry with each metal octahedrally coordinated. The cation is a Mn(II) atom possessing four EtOH and two trans oxygen ligands, the latter belonging to salicylate carboxyl groups in the anion. The Mn(II) is thus octahedrally coordinated and serves to link the anionic dimers to yield an infinite network in the crystal. **2** is the first example of a structurally characterized Mn(III) dimer containing phenoxide bridges. Magnetic moment measurements in Me_2SO yield values of 3.14 μ_B/Mn(III), indicating that the dimer remains intact in solution and that the two d^4 Mn(III) atoms are antiferromagnetically coupled.

Introduction

Biological water oxidation during plant photosynthesis represents a source of electrons for the light-driven reactions of photosystem II (PS II) of the photosynthetic apparatus and leads also to the evolution of molecular dioxygen (eq 1).[1,2] The requirement

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

for manganese (Mn) atoms in this water oxidation reaction seems well established, and it is thought that they may represent the site of binding and oxidation of the water molecules. Because of this, much effort has been concentrated on elucidating the identity of the manganese site, and significant progress has been made. In particular, the manganese atoms seem to be located in di- or tetranuclear sites with Mn⋯Mn distances of approximately 2.7 Å and a coordination shell comprised of O and/or N atoms (possibly including bridging oxygen atoms between the metals).[3-7] In the known absence of porphyrin rings, the occurrence of amino acid side-group ligation is suggested. The manganese complex is capable of cycling between five distinct oxidation levels, labelled S_0 through S_4 in the pioneering work of Kok,[8] and it is widely accepted that metal oxidation states of II, III, and/or IV are involved, although the precise nature of the redox reactions during the water oxidation cycle are by no means established with certainty.

Our objective in these laboratories is to synthesize an inorganic model of the native manganese complex to assist in elucidating the nature and mode of action of this unit during water oxidation. A necessary preliminary in this approach, however, is a better understanding of the chemistry of higher oxidation state manganese with the type of ligands likely to be binding to the metal within the natural system. This area of manganese chemistry is currently poorly investigated. We are seeking to develop this area and have been much concerned to date with exploring synthetic procedures to the desired type of compound. We herein report the results of one approach, namely the use of the permanganate ion, MnO_4^-, as a reagent for inorganic synthesis in nonaqueous solvents. We also describe the structure of the first new complex obtained from this route, containing the manganese(III) dimer unit $[Mn_2(sal)_4(pyr)_2]^{2-}$ ($salH_2$ = salicylic acid; pyr = pyridine).

Experimental Section

Picolinic acid (picH), salicyclic acid ($salH_2$), $Mn(OAc)_2 \cdot 4H_2O$, pyridine, absolute ethanol, and petroleum spirits were used as received. N-*n*-Bu_4MnO_4 was prepared from $KMnO_4$ and NBu_4Br as described[9] and used without recrystallization. All operations were carried out under aerobic conditions at ambient temperature.

Warning! There have been reports in the literature of the detonation of quaternary ammonium permanganates during drying at elevated temperatures.[10-13] A systematic study[13] has shown that salts containing unsaturated groups in the cation ($Et_3NCH_2Ph^+$, $Me_3NCH_2Ph^+$, Ph_3NMe^+, $Ph_3PCH_2CH_2PPh_3^{2+}$, Ph_4P^+) will explode at 80 °C or above. N-*n*-Bu_4^+ and NEt_4^+ salts will also decompose at these temperatures, but not explosively. We recommend appropriate care be taken in the use of organic permanganates. Further, the NEt_4^+ or N-*n*-Bu_4^+ salts should be used where possible and dried in vacuo at room temperature, as we routinely do. We have also found that N-*n*-Bu_4MnO_4 is pure enough for use without recrystallization and that storage in a refrigerator increases its stability to a slow decomposition over several weeks at room temperature to yield a brown, sticky solid.

Syntheses

$Mn(pic)_3 \cdot H_2O$ (1). A solution of $Mn(OAc)_2 \cdot 4H_2O$ (1.47 g, 6.0 mmol) and picolinic acid (3.0 g, 24.4 mmol) in EtOH (30 mL) was rapidly stirred while solid N-*n*-Bu_4MnO_4 (0.72 g, 2.0 mmol) was added in small portions over about 10 min. The resulting bright red solution soon deposited red crystals, which were collected by filtration, washed thoroughly with EtOH, and dried in vacuo. Yield: 1.88g (54%). Anal. Calcd for $C_{18}H_{14}N_3O_7Mn$: C, 49.22; H, 3.21; N, 9.57. Found: C, 49.27; H, 3.54; N, 9.14.

$[Mn(EtOH)_4][Mn_2(sal)_4(pyr)_2]$ (2). Salicylic acid (1.50 g, 10.86 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (1.00 g, 4.08 mmol) were dissolved in pyridine (20 mL) to give a clear yellow solution. This was stirred while solid (N-*n*-Bu_4)MnO_4 (0.57 g, 1.58 mmol) was added in small portions over approximately 20 min; the solution turned a deep brown-green. Overnight storage gave a brown-green precipitate, which was collected by filtration and redissolved in absolute EtOH (30 mL). Layering of an equal volume of petroleum spirits gave, after several days, dark green

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for **2**

parameter	value
formula	$C_{46}H_{50}N_2O_{16}Mn_3$
M_r	1051.74
cryst syst	monoclinic
space group	$P2_1/n$
temp, °C	-160
a, Å	13.142 (3)[a]
b, Å	16.742 (5)
c, Å	10.842 (2)
β, deg	97.15 (1)
V, Å^3	2366.89
Z	2
cryst dimens, mm	0.32 × 0.20 × 0.20
radiation (Mo Kα), Å	0.71069[b]
abs coeff, cm^{-1}	10.708
scan speed, deg min^{-1}	$4(\theta/2\theta)$
scan width, deg	1.8 + dispersion
data collcd[c]	$6° \le 2\theta \le 45°$
total no. of data	4090
no. of unique data	3103
averaging R[d]	0.028
no. of data with $F \ge 3\sigma(F)$	2461
R, %	4.90[e]
R_w, %	5.01
goodness of fit	0.998

[a] 30 reflections at -160 °C. [b] Graphite monochromator. [c] $+h,+k,\pm l$. [d] 764 unique reflections measured more than once. [e] No absorption correction performed.

crystals of **2** in 25–30% yield. This material was found suitable for structural studies. Anal. Calcd for $C_{46}H_{50}N_2O_{16}Mn_3$: C, 52.53; H, 4.79; N, 2.66. Found: C, 52.23; H, 4.78; N, 2.57. Infrared data: 3300 (m, br), 3060 (w), 2710 (w), 1600 (s), 1555 (s), 1345 (s), 1315 (s), 1230 (s), 1150 (s), 1140 (s), 1080 (m) 1070 (m), 1050 (s), 1035 (s), 1005 (m), 950 (w), 900 (s), 880 (s), 870 (m), 860 (m), 835 (s), 805 (s), 775 (s), 755 (s), 700 (s), 680 (s), 650 (s), 620 (s), 595 (s), 550 (w), 540 (w), 510 (w).

X-ray Crystallography. Data were collected at approximately -160 °C; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[14] Pertinent parameters are listed in Table I. The structure was solved by a combination of direct methods (MULTAN) and Fourier techniques. All non-hydrogen atoms were readily located, and no disorder problems were encountered. They were refined with anisotropic thermal parameters. In the latter stages, hydrogen atoms became clearly visible and were included in the refinement with isotropic thermal parameters. Hydrogen atoms H(23) through H(25) were found to be ill-behaved and were fixed in the final refinement cycle. The final values of discrepancy indices R and R_w are included in Table I.

Other Measurements. Infrared and UV/visible spectra were recorded on Perkin Elmer Model 283 and Hewlett-Packard Model 4450A spectrophotometers, as Nujol mulls and Me_2SO or DMF solutions, respectively. Solution magnetic moments were measured in dimethyl-d_6 sulfoxide solution using the Evans NMR method[15] and a spectrometer frequency of 360 MHz. Cyclic voltammograms were recorded on an IBM Model EC225 voltammetric analyzer using DMF solutions also containing tetra-*n*-butylammonium perchlorate as supporting electrolyte.

Results and Discussion

The use of permanganate for inorganic synthesis in totally (or primarily) aqueous solvents is common. However, its thermodynamic instability in this medium (eq 2) necessitates the system

$$4MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^- \qquad (2)$$

to be buffered for clean reactions, usually at pH 4.5–5.5. These aqueous acidic conditions preclude extension to ligand types of interest to us, particularly such "biologically relevant" ligands as phenoxide or imidazole. From experience we have found that reaction conditions[16] that yield discrete manganese(III) and/or manganese(IV) complexes with, e.g., bipyridine, phenanthroline, etc. yield only intractable brown precipitates (MnO_2?) with our weaker field ligands. Presumably this is due to extensive ligand protonation at the low pHs hampering reaction or instability of generated products to the acidic aqueous medium causing hydrolysis. It thus seemed desirable to avoid acidic aqueous solutions entirely and perform the reactions in organic solvents. The solubilization using crown ethers of $KMnO_4$ for organic oxidations in benzene is documented,[17] but more convenient seemed the report of tetraalkylammonium permanganates and their use for organic oxidations in pyridine, acetic acid, and dichloromethane solutions.[9,18] The potential for inorganic synthesis using these materials in such solvents seemed attractive to us. We were further encouraged by the report[19] that in DMF the first reduction potential of MnO_4^- is -0.73 V vs. SCE, a shift of approximately 1 V compared to the value in aqueous solution (+0.32 V)! This suggested that the weaker oxidizing capability in organic solvents might be manifested as cleaner, less vigorous, more controlled reactions, possibly to yield our desired products.

Having thus decided to investigate the potential of N-*n*-Bu_4MnO_4 for inorganic synthesis, our first priority was to determine whether known, stable compounds available by other methods could also be obtained by this route or whether the products under these conditions would be intractable manganese oxides. Preliminary experimentation was highly encouraging; organic solutions containing $Mn(OAc)_2 \cdot 4H_2O$ and ligand react with N-*n*-Bu_4MnO_4 to give good yields of discrete Mn complexes and *not* intractable manganese oxide polymers. With picolinic acid, for instance, the product is the known[20] Mn(III) monomer $Mn(pic)_3 \cdot H_2O$ (**1**). This reaction does not seem particularly solvent dependent; complex **1** was obtained cleanly in isolated yields of 40–70% from MeCN, EtOH, Me_2CO, and DMF. These yields are not optimized; no attempt to obtain more product from the red mother liquors was made, so actual reaction yields are probably much higher. DMF and EtOH are the solvents of choice to ensure solubility of all reactants. The use of EtOH may seem surprising given its ready oxidation by permanganate in aqueous solution. However, its oxidation in bulk EtOH appears slower and, as long as the permanganate is added to EtOH already containing the other reactants, does not pose a problem, as judged by comparison of product yields from EtOH and more "innocent" solvents. This is consistent with the lower reduction potential observed for permanganate in nonaqueous solution, as mentioned earlier. The presence of $Mn(OAc)_2$ was to allow reduction of the MnO_4^- without requiring major solvent or ligand oxidation. The reaction is not particularly sensitive to the $Mn(OAc)_2$:MnO_4^- ratio, however; ratios of 1.5:1 through 4:1 all gave compound **1** in comparable yields and purity. Obviously solvent oxidation can compensate where necessary, allowing formation of the most favorable product.

Having been encouraged by preliminary experiments that permanganate in organic media was indeed capable of giving clean reactions and discrete species, our attention now turned to use of the more interesting "biologically relevant" ligands. As a convenient substitute for tyrosine phenoxide and aspartic/glutamic acid carboxylate functions, we employed salicylic acid (2-hydroxybenzoic acid) in subsequent reactions. Preliminary screening showed clean reactions could be obtained in several solvents, but pyridine was found to yield the most tractable and crystalline products. Thus, treatment of $Mn(OAc)_2 \cdot 4H_2O$/salicylic acid solutions with N-*n*-Bu_4MnO_4 yielded homogeneous, intensely brown-green solutions from which a solid precipitated on standing. Recrystallization from EtOH/petroleum spirits gave **2** in analytical purity in nonoptimized overall yields of 25–30%. The structure of this material was determined by X-ray crystallography; the complex contains $[Mn_2(sal)_4(pyr)_2]^{2-}$ units possessing two μ-phenoxo oxygen atoms bridging two Mn(III)

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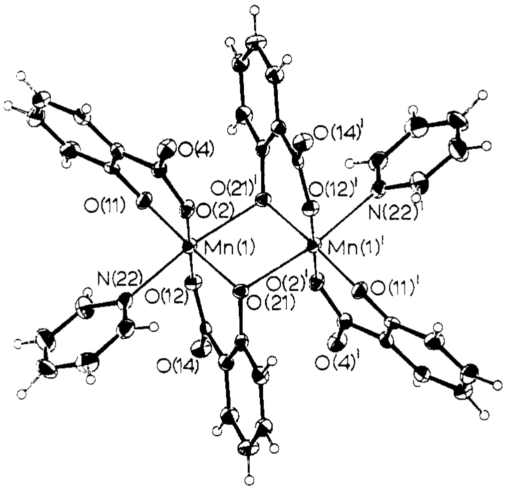

Figure 1. ORTEP projection of the "anion" of *2* showing relevant atomic labeling. Primed and unprimed atoms are related by the center of symmetry. Non-hydrogen atoms are depicted as 50% probability ellipsoids; hydrogen atoms are depicted as spheres of arbitrary size. Atoms are numbered consecutively around phenyl and pyridine ligands. Thus, one salicylate ligand is O(2)C(3)O(4)C(5)C(6)C(7)C(8)C(9)C(10)O(11).

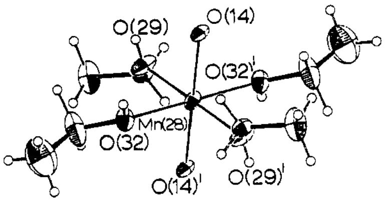

Figure 2. ORTEP projection of the "cation" of **2** showing relevant atomic labeling. The comments in the caption to Figure 1 apply to this figure also. Thus, one ethanol molecule is O(32)C(33)C(34).

Table II. Fractional Atomic Coordinates[a] and Isotropic Thermal Parameters for **2**

atom	*x*	*y*	*z*	*B*,[b] Å^2
Mn(1)	9290 (1)	732.9 (4)	5374 (1)	12
O(2)	9275 (3)	1150 (2)	3741 (3)	16
C(3)	9392 (4)	1879 (3)	3356 (5)	16
O(4)	9436 (3)	2012 (2)	2246 (3)	19
C(5)	9431 (4)	2548 (3)	4260 (5)	16
C(6)	9332 (4)	3325 (3)	3789 (5)	19
C(7)	9309 (4)	3979 (3)	4550 (6)	24
C(8)	9399 (4)	3860 (3)	5834 (6)	25
C(9)	9510 (4)	3103 (3)	6329 (5)	22
C(10)	9531 (3)	2430 (3)	5566 (5)	15
O(11)	9644 (3)	1713 (2)	6121 (3)	16
O(12)	9329 (2)	304 (2)	7022 (3)	15
C(13)	8881 (4)	−325 (3)	7388 (5)	14
O(14)	8907 (3)	−470 (2)	8526 (3)	18
C(15)	8318 (4)	−870 (3)	6471 (5)	15
C(16)	7681 (4)	−1455 (3)	6901 (5)	18
C(17)	7148 (4)	−1983 (3)	6092 (5)	21
C(18)	7243 (4)	−1945 (3)	4830 (5)	19
C(19)	7863 (4)	−1380 (3)	4393 (5)	17
C(20)	8414 (4)	−838 (3)	5199 (4)	14
O(21)	9036 (2)	−315 (2)	4707 (3)	13
N(22)	7566 (3)	951 (2)	5405 (4)	16
C(23)	6841 (4)	681 (3)	4534 (6)	22
C(24)	5811 (4)	802 (4)	4582 (6)	29
C(25)	5501 (5)	1217 (4)	5578 (7)	34
C(26)	6241 (5)	1502 (4)	6472 (6)	32
C(27)	7251 (5)	1358 (4)	6360 (6)	26
Mn(28)	10000*	0*	10000*	17
O(29)	10442 (3)	1038 (2)	8962 (3)	27
C(30)	10704 (4)	1829 (3)	9394 (5)	20
C(31)	11610 (5)	2130 (4)	8851 (7)	37
O(32)	11134 (3)	−745 (2)	9254 (4)	24
C(33)	12062 (5)	−435 (5)	8899 (8)	44
C(34)	12852 (7)	−1008 (5)	8837 (9)	65

[a] Coordinates are ×10^4 [b] Isotropic values for atoms refined anisotropically were calculated as described in ref 30. Values marked with an asterisk were not varied.

Table III. Selected Bond Lengths (Å) and Angles (deg) for **2**

a. Bonds			
Mn(1)–O(2)	1.901 (3)	Mn(28)–O(14)	2.161 (3)
Mn(1)–O(11)	1.863 (3)	Mn(28)–O(29)	2.188 (4)
Mn(1)–O(12)	1.920 (3)	Mn(28)–O(32)	2.175 (4)
Mn(1)–O(21)	1.911 (3)		
Mn(1)–O(21)′	2.320 (3)	Mn(1)···Mn(28)	5.135 (1)
Mn(1)–N(22)	2.299 (4)	Mn(1)···Mn(1)′	3.247 (1)
b. Angles			
O(2)–M(1)–O(11)	93.11 (15)	O(12)–Mn(1)–N(22)	87.62 (14)
O(2)–Mn(1)–O(12)	178.95 (15)	O(21)–Mn(1)–O(21)′	80.22 (13)
O(2)–Mn(1)–O(21)	90.24 (14)	O(21)′–Mn(1)–N(22)	171.51 (14)
O(2)–Mn(1)–N(22)	93.41 (15)	O(14)–Mn(28)–O(29)	95.94 (14)
O(11)–Mn(1)–O(12)	87.06 (14)	O(14)–Mn(28)–O(32)	93.48 (14)
O(11)–Mn(1)–O(21)	174.48 (15)	O(29)–Mn(28)–O(32)	88.50 (16)
O(11)–Mn(1)–N(22)	92.68 (15)		
O(12)–Mn(1)–O(21)′	90.38 (13)	Mn(1)–O(21)–Mn(1)′	99.78 (13)

atoms. Also present is Mn(EtOH)$_4^{2+}$, which is six-coordinate due to two additional interactions with salicylate carbonyl oxygens of the dimer, as will be described below.

Description of Structure. Fractional atomic coordinates with isotropic thermal parameters and selected bond lengths and angles are listed in Tables II and III, respectively. ORTEP projections of the "anion" and "cation" are displayed in Figures 1 and 2, respectively.

The compound crystallizes in the monoclinic space group $P2_1/n$. The dimer consists of two six-coordinate Mn(III) atoms which are 3.247 (1) Å apart and bridged by two μ-phenoxo oxygen atoms (O(21), O(21)′) from salicylate ligands, the carboxylate oxygens of which (O(12), O(12)′) are also coordinated to the metals. Each Mn(III) is additionally coordinated to a terminal bidentate salicylate (O(2), O(11), O(2)′, O(11)′), and six-coordination at the metal centers is completed by pyridine ligands. The disposition of the ligands is such as to produce a dimer of C_i symmetry; the inversion center is crystallography imposed, and as a result, the Mn_2O_2 bridging unit is perfectly planar. The geometry around each Mn(III) is distorted-octahedral, as can be seen by inspection of Table III. Angles at the metal subtended by cis and trans ligand atoms are reasonably close to theoretical values for an octahedron (90° and 180°, respectively). The biggest deviations are found in O(21)–Mn(1)–O(21)′ (80.22°) and O(21)′–Mn(1)–N(22) (171.51°), which are attributable to the asymmetry in the bridging region, as clearly visible in Figure 1. Thus, Mn(1)–O(21)′ (2.320 Å) is significantly longer than Mn(1)–O(21) (1.911 Å). This can be reasonably explained as being due to Jahn–Teller elongation, an effect for which high-spin d^4 Mn(III) is a textbook example. N(22) and O(21)′ occupy the axially elongated sites, and O(2), O(11), O(12), and O(21) occupy equatorial sites; a similar setup is observed for the other half of the dimer. This assignment is supported by comparison with bond lengths of monomeric Mn(III) systems containing equivalent linkages. In 1, containing carboxylate- and pyridine-like ligation, axial and equatorial Mn–N lengths are 2.217–2.254 and 2.059 Å, respectively, while equatorial Mn–O lengths are in the range 1.891–1.942 Å.[21] Similarly in Mn(hqn)$_3$ (hqn = 8-hydroxyquinolinate), which also contains phenoxide- and pyridine-like ligation, axial and equatorial Mn–N lengths are 2.224–2.266 and 2.057–2.058 Å, respectively, and equatorial Mn–O lengths are in the range 1.905–1.924 Å.[22] Thus, axial and equatorial Mn–N lengths are consistently 0.15–0.20 Å different, and equatorial Mn–O distances are reasonably similar among these three compounds.

The "cation" of **2** is shown in Figure 2 and consists of a six-coordinate, distorted octahedral Mn(II) atom. Two trans positions are occupied by oxygen atoms O(14) and O(14)′ from *two different* "anions", and the other four sites are occupied by ethanol

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molecules. The Mn(II) "cations" are thus bridging the Mn(III) dimer units to give an infinite network in the crystal. The high solubility of **2** in e.g. EtOH, however, suggests the cation is $[Mn(EtOH)_6]^{2+}$ in solution, together with now discrete $[Mn_2(sal)_4(pyr)_2]^{2+}$ units. This is reasonable given the weak nature of the Mn(28)–O(14) link (2.161 (3) Å). The various Mn–O distances and O–Mn–O angles around Mn(28) are all similar, as can be seen in Table III.

Complex **2** represents the first structurally confirmed example of Mn(III) centers bridged by phenoxide groups, although such an arrangement has been postulated in Mn(III) Schiff base complexes to explain magnetic moments below spin-only values.[23] Alkoxo oxygen bridged Mn(III) dimers are slightly more common. $Mn_2(OMe)_2(sah)_2$ (sah = salicylaldehyde anthraniloylhydrazonato dianion) contains two μ-OMe groups across a Mn···Mn distance of 3.144 Å; the bridges are again asymmetrical due to Jahn–Teller distortions.[24] The dimer $Mn_2(spa)_2(OAc)_2$ (H_2spa = 3-(salicylideneamino)-1-propanol) has a Mn···Mn distance of 2.869 (1) Å but a more symmetrical Mn_2O_2 core because the bridging ligands are now equatorial with respect to the Jahn–Teller elongation.[25] Also known is the bis(hydroxo)-bridged dimer $Mn_2(OH)_2(salpn)$ (salpn = *N,N'*-trimethylenebis(salicylaldiminato)). This also contains octahedral Mn centers, but structural data are limited to the Mn···Mn distance (2.72 Å).[26]

Spectroscopic and Magnetic Studies. The electronic spectrum of **2** in Me_2SO solution displays bands at 522 (ϵ_m = 215 L mol^{-1} cm^{-1}), 460 sh (274), 424 (336), 323 (8400), and 282 nm (16 500). The weaker absorptions are reasonably attributable to Mn(III) d–d transitions, while the more intense bands are attributable to LMCT; quoted ϵ_m values are per Mn(III) with contributions from, presumably, $[Mn(Me_2SO)_6]^{2+}$ ignored. In DMF solution, corresponding values are 534 (ϵ_m = 235 L mol^{-1} cm^{-1}), 460 (271), 426 (336), 323 (8400), and 282 nm (16 500). Similar spectra have been obtained in DMF for a variety of other Mn(III) complexes with salicylate.[27]

Over the concentration range 10^{-4} to 2×10^{-3} M, **2** rigorously obeys Beer's law in both DMF and Me_2SO. We reasoned that the dimeric unit could, in these good donor solvents, exist as solvated monomers formed by cleavage of the phenoxide-bridge interactions (eq 3). Such behavior has been demonstrated for

$$[Mn_2(sal)_4(pyr)_2]^{2-} + 2solv \rightleftharpoons 2[Mn(sal)_2(pyr)(solv)]^- \quad (3)$$

the dimer $[Mn_2(edt)_4]^{2-}$ (edt^{2-} = ethane-1,2-dithiolate), which contains two μ-thiolate bridges.[28] In Me_2SO, solvated monomers have been shown to be present (eq 4).[28,29] Since **2** obeys Beer's law, this suggests that eq 3 lies either completely to the left or to the right-hand side; i.e., the dimeric unit is either intact or completely dissociates into solvated monomers. To determine which possibility is occurring, we measured the magnetic moment of solutions of comparable concentration in Me_2SO-d_6 by the NMR method. The value obtained was 4.27 μ_B/Mn (7.40 μ_B/Mn_3). Subtracting the expected contribution of a high-spin Mn(II) ion leads to a value of 3.14 μ_B/Mn(III). This is much less than expected for an isolated Mn(III) (approximately 4.90 μ_B) as would be found in a solvated monomer and suggests that the dimeric unit remains intact in solution, allowing antiferromagnetic coupling between the two Mn(III) centers. Some support for the above is found in the magnetic moments of the Mn(III) Schiff base complexes thought to be dimeric.[23] Somewhat similar moments in the range 3.40–3.52 μ_B per Mn(III) were obtained. These slightly higher values may be due to structural differences from the structure of **2**, such as longer Mn···Mn distances, but in the absence of structural data, it is difficult to make further comment at the present time. To avoid the complicating presence of the Mn(II) center in **2**, we have attempted to isolate the anion with quaternary ammonium or phosphonium cations. However, when these other cations are included in the reaction mixture, the precipitated product is still **2**. Presumably this must be the most insoluble product. Similarly we have been unable as yet to remove the Mn(II) from preformed **2**. Such attempts are continuing for we wish to investigate the variable-temperature magnetic properties of the $[Mn_2(sal)_4(pyr)_2]^{2-}$ dimer unit and quantitate the strength of the antiferromagnetic interaction.

$$[Mn_2(edt)_4]^{2-} + 2Me_2SO \rightarrow 2[Mn(edt)_2(Me_2SO)_n]^- \quad (4)$$

The utility of MnO_4^- in nonaqueous solvents for the synthesis of complex **2** is emphasized by the rapid hydrolysis of the latter to an intractable brown solid when dissolved in water. This rationalizes the failure of the aqueous MnO_4^- route and generally supports the need to avoid this medium in attempting to use MnO_4^- to prepare higher oxidation state Mn complexes with weak field ligands such as salicylate.

Finally, electrochemical studies on **2** have shown that it is incapable of reversible redox reactions; only an irreversible oxidation at +0.93 V vs. NHE is observed, assigned to oxidation of the Mn(II) center. The lack of reversible redox chemistry and the large Mn···Mn separation suggest that $[Mn_2(sal)_4(pyr)_2]^{2-}$ is not a model of the redox-active Mn cluster involved in water oxidation in photosynthesis. Nevertheless, the synthesis of **2** represents an important step forward in the development of Mn chemistry with ligand types likely to be occurring at this native site, progress which will hopefully lead to the synthesis of a satisfactory model. With this objective in mind, further studies employing permanganate in nonaqueous solvents are continuing.

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Registry No. **1**, 15037-07-7; **2**, 100569-15-1; $Mn(OAc)_2$, 638-38-0; N-*n*-Bu_4MnO_4, 35638-41-6.

Supplementary Material Available: Tables of fractional coordinates for all atoms, anisotropic thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (7 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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