$\mu$-oxo groups (2.050 Å) is 0.047 Å shorter than the average trans distance (2.097 Å). This elongation trans to the $\mu$-oxo groups for the Mn(IV) ion is often observed for oxo-bridged species,[22] including **1**. Unlike the situation for **1** and **3**, mixed-valence complexes **2** and $[(TACN)Mn(\mu\text{-}O)_2(\mu\text{-}OAc)Mn(TACN)]^{3+}$ (**4**)[12a] do not have distinguishable Mn(III) and Mn(IV) ions.

Cyclic voltammetry of **3** reveals a quasi-reversible redox wave with $E_a = 0.87$ V, $E_c = 0.79$ V, and $E_{1/2} = 0.83$ V (vs Ag/Ag$^+$), corresponding to the III, IV/IV,IV couple and a wave at $E_a = 0.15$ V, $E_c = -0.02$ V, and $E_{1/2} = 0.085$ V, due to the III,IV/III,III couple.[23] The former couple for **1**, and **2**, lies at significantly higher values: $E_{1/2} = 1.25$ and 1.26 V, respectively.[7] The EPR spectrum of **3**, displayed in Figure 2, bears a remarkable resemblance to that for a recently reported species suspected of being a peroxy-bridged $Mn^{II}Mn^{III}$ complex.[24] Preliminary simulations for the 16-line pattern in Figure 2 yielded spectral parameters $A_1 = 150 \times 10^{-4}$ cm$^{-1}$ and $A_2 = 78 \times 10^{-4}$ cm$^{-1}$, in good agreement with hyperfine values derived for **1**, **2**, and **4**.[6,12a] Anisotropy is indicated by splitting in the high-field region of the spectrum; thus, an improvement in the simulation resulted by using parameters $g_{x,y} = 1.961$, $g_z = 1.953$, $A_{1x} = A_{1y} = 150 \times 10^{-4}$ cm$^{-1}$, $A_{1z} = 128 \times 10^{-4}$ cm$^{-1}$, and $A_{2x} = A_{2y} = A_{2z} = 69 \times 10^{-4}$ cm$^{-1}$. Magnetic susceptibility measurements on a powdered sample of **3** were fit to the expression for $\chi_M$ vs $T$ derived from the isotropic spin-exchange Hamiltonian,[25] $H' = -2JS_1S_2$, with $S_1 = 2$, $S_2 = {}^3/_2$, $g = 1.958$, and $J = -146$ cm$^{-1}$.[26] Antiferromagnetic interactions of this magnitude between Mn(III) and Mn(IV) ions were also observed for **1** (−150 cm$^{-1}$)[6] and **2** (−134 cm$^{-1}$,[6] −148 cm$^{-1}$ [11]). An IR absorption band at 694 cm$^{-1}$ for a $CH_3CN$ solution of **3** can be tentatively assigned to a vibration of the $Mn_2O_2$ core. IR spectra of **1** and **2**[7] display analogous bands at 688 and 686 cm$^{-1}$, respectively. The electronic absorption spectrum of **3** in $CH_3CN$[27] is similar to that of **1**, with the exception of a broad band at 800 nm that is observed for **1** but not for **3**. This near-IR absorption in **1** has been assigned to an intervalence transition.[7]

In conclusion, the second example of a complex containing a $[Mn^{III}(\mu\text{-}O)_2Mn^{IV}]^{3+}$ core for which the Mn(III) and Mn(IV) ions can be clearly distinguished in the solid state has been discovered. The principal differences between $[Mn_2O_2(tren)_2]^{3+}$ (**3**) and the bpy or phen dimers (**1**, **2**) are (i) the III,IV/IV,IV redox couple is shifted to a lower potential by 0.42 V for **3** compared to **1**, (ii) compound **3** has a greater reactivity toward dioxygen and/or water, and (iii) an absorption band in the near-IR region for **1** is not present in the same position for **3**. Further model studies of the sort presented here will be directed toward an understanding of the role of manganese in the oxygen-evolving complex of photosystem II and manganese aggregation chemistry in general.

**Acknowledgment.** We thank Jean-Luc Zimmermann for the simulation of the EPR spectrum. This work was supported by Grant No. GM382751-01 from the National Institutes of General Medical Sciences.

**Supplementary Material Available:** A table of atomic positional and thermal parameters for **3**·EtOH (2 pages). Ordering information is given on any current masthead page.

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[21] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 4th ed.; Wiley: New York, 1980; pp 678-682.

[22] Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653-3667 and references therein.

[23] There was evidendce of adsorption of **3** to the Pt electrode surface used for these measurements.

[24] Mabad, B.; Tuchagues, J.-P.; Hwang, Y. T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 2801-2802.

[25] O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 204-283.

[26] Other parameters used in the fit include a diamagnetic correction of 444 × $10^{-6}$ cgs mol$^{-1}$, a temperature-independent paramagnetism of 120 × $10^{-6}$ and 180 × $10^{-6}$ cgs mol$^{-1}$ for Mn(III) and Mn(IV), respectively, and a 3% paramagnetic ($Mn^{2+}$) impurity.

[27] Electronic spectrum in $CH_3CN$ [λ, nm (ε, M$^{-1}$ cm$^{-1}$)]: 380 (1170), 428 sh, 526 sh, 548 (440), 590 sh, 638 sh, 680 (570).

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## Synthesis and Structures of $[(C_6H_5)_4P]_2[M(CO)_4Te_4]$ (M = Cr, W), Containing a Polytelluride Ligand Derived from a Soluble Zintl Anion

*Sir:*

The chemistry of compounds containing inorganic chalcogenide ligands has recently been reviewed by several authors,[1-3] and notable by their absence are rings containing tellurium atoms. The ligand chemistry of the polysulfides[1,3] is reasonably well developed, and there have been several polyselenides reported.[4-6] However the ligand chemistry of tellurium in general has received little study, and the only metal polytellurides have been obtained through extraction of alloys containing Zintl phases.[7,8] We report here the first examples of polytelluride rings chelating to transition metals.

The primary synthetic approach to metal polysulfides and polyselenides is usually to dissolve $H_2S$ (or $H_2Se$) in aqueous base to generate polysulfide solutions, which are then reacted with appropriate metal compounds, usually a metal–oxo or metal sulfide compound. Often the initial product is a tetrathiometalate.[9] However this is not a convenient route to tellurides because of the instability of $H_2Te$. In addition, solutions containing tellurides are extremely air sensitive and generally unstable. We have found, however, that extraction of the Zintl phases, such as $K_2Te_3$ or $K_2Te_4$, into basic solvents like DMF affords a convenient method of generating solutions containing polytellurides suitable for reaction with transition-metal complexes.[10] This is similar to the approach used to generate several new organotellurium compounds.[11-13]

The synthesis of $[(C_6H_5)_4P]_2[M(CO)_4Te_4]$ (M = Cr (**Ia**) and W (**Ib**)) is carried out by typically reacting 0.200 g (0.340 mmol) of $K_2Te_4$ with 1 equiv of the appropriate metal carbonyl in 10 mL

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[1] Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

[2] Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1986; p 680.

[3] Diemann, E.; Müller, A. *Coord. Chem. Rev.* **1976**, *10*, 79.

[4] Strasdeit, H.; Krebs, B.; Henkel, G. *Inorg. Chim. Acta* **1984**, *89*, L11.

[5] Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823.

[6] Wardle R. W. M.; Chau, C.-N.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1859.

[7] Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 432.

[8] Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 433.

[9] Müller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

[10] $K_2Te_4$ is prepared by combining 5.0 g (0.039 mol) of elemental tellurium with 0.80 g (0.020 mol) of elemental potassium in a flask equipped with a Teflon valve and a glass-coated stirbar under argon. Approximately 30 mL of dry $NH_3$ is added to the flask by distillation. The mixture is stirred for 3 h at −78 °C and the $NH_3$ removed from the intense purple solution. The resulting gray microcrystalline powder can be stored indefinitely under argon. The inky blue $K_2Te_2$ and blood red $K_2Te_3$ are prepared in similar fashion by using appropriate stoichiometries.

[11] Goodman, M. M.; Knapp, F. F. *Organometallics* **1983**, *2*, 1106.

[12] Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organomet*, **1983**, *2*, 549.

[13] Sandman, D. J.; Stark, J. C.; Acampora, L. A.; samuelson, L. A.; Allen, G. W.; Jansen, S.; Jones, M. T.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 1.

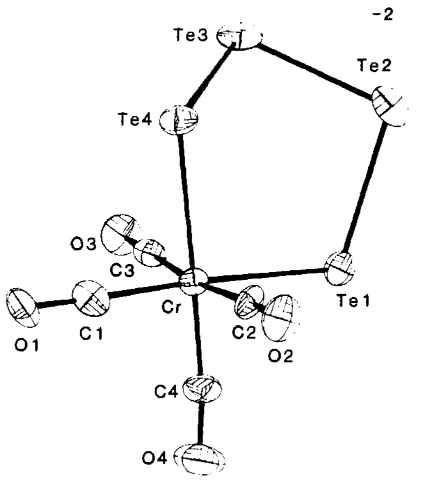

**Figure 1.** View of the $Cr(CO)_4Te_4$ fragment in Ia, showing the tetratellurium fragment chelated to the metal carbonyl fragment.

**Table I.** Selected Distances (Å) and Angles (deg) for $[M(CO)_4Te_4]^{2-}$

| | M = Cr | M = W |
|---|---|---|
| | Distances | |
| Te(1)-Te(2) | 2.750 (1) | 2.764 (2) |
| Te(2)-Te(3) | 2.717 (1) | 2.719 (1) |
| Te(3) - Te(4) | 2.705 (1) | 2.703 (1) |
| M-Te(1) | 2.753 (2) | 2.856 (1) |
| M-Te(4) | 2.699 (2) | 2.819 (1) |
| M-C(4) | 1.840 (14) | 2.029 (11) |
| M-C(3) | 1.768 (14) | 1.942 (11) |
| M-C(2) | 1.798 (13) | 1.964 (13) |
| M-C(1) | 1.856 (14) | 2.040 (12) |
| C(4)-O(4) | 1.174 (14) | 1.144 (13) |
| C(3)-O(3) | 1.189 (13) | 1.174 (13) |
| C(2)-O(2) | 1.162 (13) | 1.181 (17) |
| C(1)-O(1) | 1.160 (13) | 1.125 (15) |
| | Angles | |
| Te(1)-Te(2)-Te(3) | 97.45 (5) | 98.7 (1) |
| Te(2)-Te(3)-Te(4) | 97.99 (4) | 98.6 (1) |
| M-Te(1)-Te(2) | 109.62 (5) | 108.7 (1) |
| M-Te(4)-Te(3) | 103.42 (5) | 102.5 (1) |
| Te(1)-M-Te(4) | 98.75 (6) | 97.3 (1) |
| C(4)-M-C(3) | 90.7 (6) | 91.8 (4) |
| C(3)-M-C(2) | 91.5 (5) | 91.5 (5) |
| C(2)-M-C(1) | 90.3 (6) | 90.6 (5) |
| C(4)-M-C(1) | 173.4 (5) | 175.9 (6) |
| C(3)-M-Te(1) | 172.5 (4) | 173.1 (3) |
| C(2)-M-Te(4) | 175.6 (4) | 176.8 (3) |
| C(4)-M-Te(1) | 83.8 (4) | 82.2 (3) |
| C(4)-M-Te(4) | 89.4 (4) | 90.5 (3) |
| C(1)-M-Te(1) | 91.4 (4) | 94.6 (3) |
| C(1)-M-Te(4) | 86.9 (4) | 87.3 (3) |
| C(2)-M-Te(1) | 84.7 (4) | 85.4 (3) |
| C(3)-M-Te(4) | 86.3 (4) | 86.1 (3) |

of DMF for 3 days at room temperature, or overnight at 90 °C, under rigorously anaerobic conditions. Addition of 2 equiv of $(C_6H_5)_4PBr$ and an equal volume of THF to the red-brown solution produces KBr as a precipitate from the reaction mixture. Filtration, followed by slow addition of a second volume of THF and storage at 4 °C overnight, results in isolation of analytically pure dark brown crystals of the desired product in reasonable (50%) yield.[14]

$$M(CO)_6 + K_2Te_4 \rightarrow (CO)_4MTe_4^{2-} + 2CO$$

$$(CO)_4MTe_4^{2-} + 2(C_6H_5)_4PBr \rightarrow [(C_6H_5)_4P]_2[(CO)_4MTe_4]$$

Ia, M = Cr
Ib, M = W

The reaction of $K_2Te_4$ with $Mo(CO)_6$ under the same conditions gave solutions with similar IR spectra as the other metals, but attempts at isolation resulted only in oily solids and were not pursued. The use of $K_2Te_3$ or $K_2Te_2$ in place of $K_2Te_4$ with any of the metal carbonyls seems to have no effect on either the nature or amount of product. This effect has been noted previously in reactions involving polysulfide solutions and transition-metal complexes.[1]

Both compounds were characterized by elemental analysis, IR spectroscopy[14] and single-crystal X-ray diffraction. The IR spectra of each compound showed four bands in the carbonyl stretching region, as expected for localized $C_{2v}$ symmetry around the metal atoms. The bands are centered around 1880 cm$^{-1}$, which is typical for a metal carbonyl dianion.[15]

The single-crystal X-ray structures of the two compounds indicate that they are isostructural.[16] The black crystals are monoclinic, space group $P2_1/c$, with $Z = 4$. Ia contains a solvent molecule of THF and Ib contains a molecule of DMF. Each compound consists of two well-separated $(C_6H_5)_4P^+$ counterions and a discrete dianion, containing a $M(CO)_4$ fragment to which a $Te_4^{2-}$ chain has been chelated through both terminal tellurium atoms (see Figure 1). This creates a five-membered ring that is in an envelope conformation with the transition-metal carbonyl fragment in a basal position. The metal tellurium fragment of the envelope (Te(4)-M-Te(1)-Te(2)) is nearly planar and the Te-Te-Te-Te torsion angle is 50°. This geometry is common for systems containing four-membered sulfur rings chelated to a metal center, i.e. $Cp_2WS_4$[17,18].

The tellurium to chromium distances average 2.727 Å and those to tungsten average 2.838 Å (see Table I). The distance between the metal and Te(1) (the base of the envelope) is longer by about 0.05 Å than that between the metal and Te(4) in each case. The average distances compare reasonably to the other molecular metal tellurium distances reported, (2.765 (4) Å for Cr-Te[19] and 2.839 (2) Å for W-Te[20]). In most of the five-membered metal-sulfur rings reported, the S-S distance adjacent to the metal-sulfur bond is longer than normal. This has been attributed to the presence of a $\pi$-overlap contribution to the metal-sulfur bond, with concomitant lengthening of the S-S bond.[18,21] This does not appear to be the case in the present system, presumably due to the poorer overlap of orbitals of the large tellurium atoms with the metal. There also appears to be a noticable electronic influence exerted by the tellurium ligands upon the carbonyl ligands. The carbonyls trans to the tellurides have shorter M-C distances and longer C-O distances. This suggests that tellurides can act as moderate $\pi$ donors, enhancing the metal to CO back-donation.

In each case, the Te-M-Te angle is about 99°, presumably due to the large size of the tellurium atoms as well as ring strain. Interestingly, however, the CO ligands do not bend away from the tellurium atoms or deviate from $C_{2v}$ symmetry. Rather, they remain almost 90° apart, and the Te-M-CO angle is somewhat decreased (to about 87°). It should be noted that there are very few polychalcogenide rings chelated to metal carbonyls.

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(14) IR ($\nu$(CO), cm$^{-1}$): for Ia, 1951 (m), 1850 (s), 1821 (s), 1778 (m); for Ib, 1971 (m), 1950 (s), 1821 (s), 1780 (m). Anal. Calcd for Ia: C, 46.31; H, 3.32. Found: C, 45.91; H, 3.45. Calcd for Ib: C, 42.40; H, 3.04. Found: C, 42.17, H, 3.09.

(15) Ruff, J. K. *Inorg. Chem.* **1969**, *8*, 86.

(16) Crystal data for $[(C_6H_5)_4P]_2[Cr(CO)_4Te_4]\cdot THF$: space group $P2_1/c$, $Z = 4$, $\mu = 24.2$ cm$^{-1}$, $d = 1.74$ g/cm$^3$, $a = 22.122$ (4) Å, $b = 13.096$ (8) Å, $c = 20.850$ (8) Å, $\beta = 115.76$ (3)°, $V = 5440$ (8) Å$^3$, $T = 293$ K, 9551 reflections read to $2\theta$(Mo K$\alpha$) = 50°, with R = 0.046 for 3903 reflections of $F_o^2 > 3\sigma(F_o^2)$. Crystal data for $[(C_6H_5)_4P]_2[W(CO)_4Te_4]\cdot DMF$: space group $P2_1/c$, $Z = 4$, $\mu = 44.1$ cm$^{-1}$, $d = 1.91$ g/cm$^2$, $a = 22.016$ (4) Å, $b = 13.059$ (3) Å, $c = 20.949$ (4) Å, $\beta = 116.15$ (1)°, $V = 5406$ (1) Å$^3$, $T = 143$ K, 7019 reflections read to $2\theta$(Mo K$\alpha$) = 45°, with $R = 0.038$ for 4651 reflections of $F_o^2 > 3\sigma(F_o^2)$.

(17) Davis, B. R.; Bernal, I.; Kopf, H. *Angew. Chem., Int. Ed.* Engl. **1971**, *12*, 921.

(18) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenzinger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.

(19) Lappert, M. F.; Martin, T. R.; McLaughlin, G. G. *J. Chem. Soc., Chem. Commun.* **1980**, 635.

(20) Scheidsteger, O.; Huttner, G.; Dehnicke, K.; Pebler, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 428.

(21) Coucouvanis D.; Hadjikyriacou, A. Draganjac, M.; Kanatzidis, M. G. Ileperuma, O. *Polyhedron* **1986**, *5*, 349.

The fact that the nature of the polytelluride used as starting material does not affect the product suggests that there are facile and complex equilibria in solution. This is also in accord with NMR investigations of polyselenide and telluride solutions.[22] However, the simplicity of the reactions suggests that polytellurides extracted from Zintl phases are useful reagents for introducing polytellurium chains into metal complexes.

**Acknowledgment.** We are indebted to Chuck Campana and Nicolet Corp. for structural data on Ib. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

**Registry No.** Ia·THF, 112817-27-3; Ib·THF, 112817-31-9; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $K_2Te_3$, 67488-76-0; $K_2Te_2$, 78547-42-9; $K_2Te_4$, 112817-28-4; $Mo(CO)_6$, 13939-06-5.

**Supplementary Material Available:** Tables of atomic coordinates and isotropic temperature factors, cation and solvent distances and angles, anisotropic temperature factors, and hydrogen atom parameters (17 pages); a table of observed and calculated structure factors (63 pages). Ordering information is given on any current masthead page.

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(22) Schrobilgen G. J.; Bjorgvinnson, M., in press.

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## Synthesis and Characterization of a Mixed-Valence Binuclear Manganese(II,III) Complex of a Septadentate Polyimidazole Ligand[1]

*Sir:*

A multinuclear manganese center is known to play an integral role in the water-oxidizing complex of photosystem II (PS(II)).[2] The manganese center is capable of cycling between five oxidation levels ($S_0$–$S_4$) during the catalytic water oxidation cycle.[3] Two to four Mn ions are thought to participate directly in the oxidation process, and the $S_2$ state of the complex shows substantial Mn hyperfine structure in the EPR spectrum, which has been used to study the electronic structure of the manganese aggregate.[4] Because high-resolution structural data on the Mn site in PS(II) and other manganese-containing proteins are absent, efforts have focused on preparing and characterizing low molecular weight inorganic analogues[5-9] that mimic the spectral properties of the various $S_n$ states. Therefore low molecular weight polymanganese complexes containing biologically relevant ligands such as imidazole, phenolates, and acetates that exhibit numerous manganese hyperfine EPR lines are of interest.

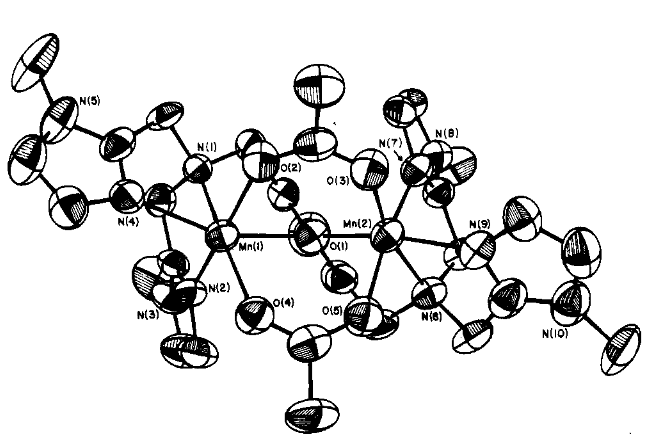
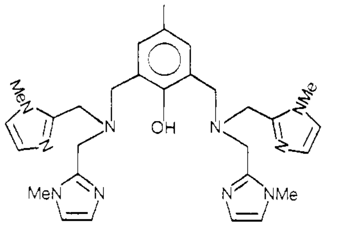


**Figure 1.** Structure of $[Mn_2(L\text{-}Im)(\mu\text{-}OAc)_2]^+$. The view is down the pseudo-2-fold axis of the dimer. Selected bond distances (Å) and angles (deg) are as follows: Mn(1)–O(1) = 2.258 (6); Mn(1)–O(2) = 2.107 (6); Mn(1)–O(4) = 2.091 (6); Mn(1)–N(1) = 2.364 (6); Mn(1)–N(2) = 2.186 (7); Mn(1)–N(4) = 2.229 (7); Mn(2)–O(1) = 1.887 (5); Mn(2)–O(3) = 1.995 (6); Mn(2)–O(5) = 2.036 (6); Mn(2)–N(6) = 2.270 (8); Mn(2)–N(7) = 2.100 (7); Mn(2)–N(9) = 1.998 (7); Mn(1)–O(1)–Mn(2) = 116.8 (3).

In the present study we wish to report the synthesis and characterization of a valence trapped binuclear mixed-valence Mn(II,III) complex prepared from a new septadentate ligand, HL-Im = 2,6-bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol (I).[10] This ligand should provide a good



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(1) Complete description of crystal structure and properties of $[Mn_2(L\text{-}Im)(\mu\text{-}OAc)_2](ClO_4)_2$ will be described in a full paper submitted for publication in *Inorg. Chem.*

(2) (a) Sauer, K. *Acc. Chem. Res.* **1980**, *13*, 249. (b) Dismukes, G. C. *The Organization and Function of Manganese in the Water-Oxidizing Complex of Photosynthesis*; Academic: New York, 1986; Chapter 16, p 275. (c) Dismukes, G. C *Photochem. Photobiol.* **1986**, *43*, 99. (d) Kambara, T.; Govindjee. *Proc. Natl. Acad. Sci. U.S.A* **1985**, *82*, 6119. (e) Amesz, J. *Biochim.* Biophys. *Acta* **1983**, *726*, 1. (f) Webber, A. N.; Spencer, L.; Sawyer, D. T.; Heath, R. L *FEBS Lett.* **1985**, *189*, 258. (g) Livornes, J.; Smith, T. D. *Struct. Bonding (Berlin)* **1982**, *48*, 1.

(3) (a) Srinvasan, A. N.; Sharp, R. R. *Biochim. Biophys. Acta* **1986**, *850*, 211. (b) Goodin, D. B.; Yachandra, V. K.; Britt, R. D.; Sauer, K.; Klein, M. P. *Biochim. Biophys. Acta* **1984**, *767*, 209. (c) Kok, B.; Forbush, B.; McGloin, M. *Photochem. Photobiol.* **1970**, *11*, 457.

(4) (a) Dismukes, G. C.; Siderer, Y. *Proc. Natl. Acad. Sci. U.S.A* **1981**, *78*, 274. (b) Brudvig, G. W.; Casey, J. L.; Sauer, K. *Biochim. Biophys. Acta* **1983**, *723*, 366. (c)Hansson, Ö.; Andréasson, L.-E. *Biochim. Biophys. Acta* **1982**, *679*, 261. (d) Zimmerman, J.-L.; Rutherford, A. W. *Biochemistry* **1986**, *25*, 4609. (e) dePaula, J. C.; Brudwig, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 2643. (f) dePaula, J. C.; Innes, J. B.; Brudvig, G. W. *Biochemistry* **1985**, *24*, 8114. (g) dePaula, J. C.; Beck, W. F.; Brudvig, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 4002. (h) Hansson, Ö.; Aasa, R.; Vänngard, T. *Biophys. J.* **1987**, *51*, 825.

(5) (a) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041. (b) Mabad, B.; Tuchagues, J.-P.; Hwang, Y. T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 2801. (c) Mabad, B.; Cassoux, P.; Tuchagues, J.-P.; Hendrickson, D. N. *Inorg. Chem.* **1986**, *25*, 1420.

(6) (a) Wieghardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc. Chem. Commun.* **1985**, 346. (b) Wieghardt, K.; Bossek, U.; Gebert, W. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 328. (c) Wieghardt, K.; Bossek, U.; Zsolnai, L.; Huttner, G.; Blondin, G.; Girerd, J.-J.; Babonneau, F. *J. Chem. Soc., Chem. Commun.* **1987**, 651.

(7) (a) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1980**, *19*, 492. (b) Bodini, M. E.; Willis, L. A.; Riechel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1538. (c) Maslen, H. S.; Waters, T. N. *J. Chem. Soc., Chem. Commun.* **1973**, 760. (d) Matsushita, T.; Shono, T. *Polyhedron* **1983**, *2*, 613. (e) Okawa, H.; Honda, A.; Nakamura, M.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1985**, 59.

(8) (a) Pavacik, P. S.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1986**, *25*, 996. (b) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236. (c) Vincent, J. B.; Christou, G. *Inorg. Chim. Acta* **1987**, *136*, L41. (d) *Pavacik*, P. S.; Huffman, J. C.; Christou, G. *J. Chem. Soc. Chem. Commun.* **1986**, 43.

(9) (a) Cooper, S. R.; Dismukes, G. C.; Klein, M. P.; Calvin, M. *J. Am. Chem. Soc.* **1978**, *100*, 7248. (b) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435. (c) Mathur, P.; Crowder, M.; Dismukes, G. C. *J. Am. Chem. Soc.* **1987**, *109*, 5227. (d) Kessissoglou, D. P.; Li, X.; Butler, W. M.; Pecoraro, V. L. *Prog. Photosynth. Res.* **1987**, *1*, 725. (e) Kessissoglou, D. P.; Li, X.; Butler, W. M.; Pecoraro, V. L. *Inorg. Chem.* **1987**, *26*, 2487.

0020-1669/88/1327-0971$01.50/0