3502 *J. Am. Chem. Soc.* **1995,** *117,* 3502−3509

# An Unusual Transition Metal Cluster Containing a Seven Metal Atom Plane. Syntheses and Crystal Structures of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$, $Mn_3(THF)_2(CO)_{10}$, and $[Mn(THF)_6][Mn(CO)_5]_2$

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*Received July 21, 1994*⊗

**Abstract:** Dimanganese decacarbonyl reacts with trimethylaluminum in a mixture of hexane and tetrahydrofuran to produce $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (**1**; THF = tetrahydrofuran) and the unstable compounds $Mn_3(THF)_2(CO)_{10}$ (**2**) and $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**). The crystal structure of **1** is made up of two $Mn_7(THF)_6(CO)_{12}^-$ anions, each of which is coordinated to an isolated $Mn^{2+}$ cation via three carbonyl oxygens to give an octahedral coordination geometry about the cation. The framework of each $Mn_7(THF)_6(CO)_{12}^-$ anion consists of a ring of six manganese atoms, all of which are attached to a seventh manganese in the center of the ring to form a planar $Mn_7$ unit. The six-membered ring is made up of alternating $Mn(CO)_4$ and $Mn(THF)_2$ groups, and if metal−metal bonds to the central manganese are ignored, the former have approximate octahedral coordination while the latter have somewhat distorted tetrahedral geometries. The complex crystallizes in two forms, one form that contains two molecules per formula unit of the tetrahydrofuran adduct of trimethylaluminum, and another form in which the trimethylaluminum adduct is absent. Crystal data for $[Mn][Mn_7(THF)_6(CO)_{12}]_2 \cdot 2Al(CH_3)_3THF$: monoclinic space group $P2_1/c$ (No. 14), $a = 13.630(3)$ Å, $b = 24.847(5)$ Å, $c = 17.645(4)$ Å, $\beta = 106.01(3)^\circ$, $Z = 2$, $R = 6.56\%$, $R_w = 6.75\%$. Crystal data for $[Mn][Mn_7(THF)_6(CO)_{12}]_2$: monoclinic space group $P2_1/c$ (No. 14), $a = 18.268(2)$ Å, $b = 20.395(4)$ Å, $c = 15.143(2)$ Å, $\beta = 103.064(8)^\circ$, Z = 2, $R = 8.75\%$, $R_w = 9.55\%$. The structure of **2** consists of two $Mn(CO)_5$ groups connected by metal−metal bonds to a central $Mn(THF)_2$ unit, and **3** consists of isolated $[Mn(THF)_6]^{2+}$ and $[Mn(CO)_5]^-$ ions. Crystal data for $Mn_3(THF)_2(CO)_{10}$ (**2**): monoclinic space group $P2_1/n$ (No. 14), a = 8.9394(7) Å, b = 16.795(2) Å, c = 16.048(2) Å, $\beta = 95.239(8)^\circ$, Z = 4, $R = 4.26\%$, $R_w = 3.85\%$. Crystal data for $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**): triclinic space group $P\bar{1}$ (No. 2), $a = 10.352(1)$ Å, $b = 10.443(1)$ Å, $c = 19.552(3)$ Å, $\alpha = 83.86(1)^\circ$, $\beta = 88.14(1)^\circ$, $\gamma = 86.037(9)^\circ$, Z = 2, $R = 6.57\%$, $R_w = 9.07\%$.

## Introduction

Over the past 30 years the study of transition metal clusters has grown to encompass several hundred compounds ranging in size from the minimum of 2 to well over 50 metal atoms.[1] The impetus for the study of these compounds has come from the enormous importance of metal-based catalysts in industrial chemical processes. Metal clusters have been used as homogeneous catalysts[2] and have been examined both as model systems[3] and as precursors[4] for heterogeneous catalysts. As a class these compounds have presented many challenges to conventional bonding theory, and although great progress has been made in describing the electronic environments of the metal atom frameworks,[5] the nature of the metal−metal bonding in many molecules is still not fully understood.

Although the great majority of large transition metal clusters have frameworks that are best described as some variant of a three-dimensional polyhedron, there are a number of examples of "raft" complexes that have two-dimensional networks of metals. This geometry is well-represented for five and six metal clusters, but it is still very unusual for clusters of higher nuclearity.[5] Most of these planar compounds are either ruthenium or osmium clusters, or contain a mixture of a transition metal and a coinage metal (Cu, Ag, or Au).

There are many high-nuclearity complexes of manganese containing five or more metals; however, all but three consist of aggregations of manganese cations held together by anionic bridging ligands rather than manganese−manganese bonds. The low-valent organometallic clusters are limited to $Mn_6(CO)_9\{\mu\text{-}OP(OEt)_3\}_9$[6] and $Mn_7(\mu_3\text{-}OH)_8(CO)_{18}$,[7] neither of which has any metal−metal bonds, the $[In\{Mn(CO)_4\}_5]^{2-}$ anion,[8] and $[(\mu_4\text{-}In)\{(\mu\text{-}H)Mn_3(CO)_{12}\}_2]^{2-}$,[9] which consists of two $Mn_3$ triangles linked by a bridging indium atom. To our knowledge the $[In\{Mn(CO)_4\}_5]^{2-}$ anion is presently the only reported example of a manganese cluster that contains more than three metal atoms connected by manganese−manganese bonds.

In the course of preparing compounds containing bonds between low-valent transition metals and the heavier group 13

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⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1995.

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elements (Al, Ga, In, Tl), we carried out several reactions between trimethylaluminum and dimanganese decacarbonyl in an attempt to form an aluminum–manganese cluster. Surprisingly, these reactions produced the very unusual manganese complexes $[Mn][Mn_7(THF)_6(CO)_{12}]_2$, $Mn_3(THF)_2(CO)_{10}$, and $[Mn(THF)_6][Mn(CO)_5]_2$ (THF = tetrahydrofuran). All three compounds contain "lightly stabilized" manganese atoms coordinated to tetrahydrofuran, and the first complex contains a seven metal atom plane in which several of the atoms are in very interesting coordination environments that involve unusual metal–metal interactions.

## Experimental Section

**General Methods.** All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or under argon in a drybox. Dimanganese decacarbonyl and trimethylaluminum were obtained from Strem Chemicals, Inc. and Ethyl Corp., respectively, and were used as received. Solvents were freshly distilled under an atmosphere of dry nitrogen from potassium (hexane), sodium benzophenone ketyl (tetrahydrofuran, diethyl ether), or calcium hydride (dichloromethane, acetonitrile) before use. Infrared spectra were routinely obtained on a Perkin-Elmer 1600 series Fourier-transform spectrophotometer. Sample cells with $CaF_2$ windows were used for solution spectra. $^1H$ NMR spectra were recorded on an IBM AF-200 (200 MHz) Fourier-transform spectrometer and were calibrated relative to acetonitrile-$d_2$ resonances. Melting points were measured under nitrogen in sealed capillaries and are uncorrected. Elemental analyses were performed by Desert Analytics (Tuscon, AZ) and Schwarzkopf Microanalytical Laboratory, Inc. (Woodside, NY).

**Preparation of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (1).** A solution of $Al(CH_3)_3$ (4.45 g, 61.7 mmol) in dry tetrahydrofuran (20 mL) was added to $Mn_2(CO)_{10}$ (2.28 g, 5.85 mmol) at 25 °C. The mixture was heated to reflux for 50 h to produce a red powder and a dark red-orange solution. After being cooled to 25 °C the solution was removed using a cannula equipped with a fritted glass disk. The red powder was dissolved in dry tetrahydrofuran (60 mL) and the resulting solution was filtered via cannula. Volatile materials were then removed under vacuum to yield $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ as a red powder. The amount of tetrahydrofuran in the dry compound is variable, and $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ can be regenerated unchanged when the complex is redissolved in THF. Dark red crystals of the complex can be obtained from THF/hexane solutions; however, in the absence of solvent they rapidly lose crystallinity (as determined by X-ray diffraction). A qualitative test for the presence of aluminum[10] was negative. The compound burns readily when the solid is exposed to air. Yield: 0.9844 g (53.4% based on manganese and calculated using the formula $[Mn][Mn_7(THF)_6(CO)_{12}]_2$). Melting point: the compound decomposes over the temperature range 215–220 °C. Infrared spectrum ($\nu_{CO}$, THF solution): 2010 (w), 1933 (w), 1899 (s), 1840 (s), 1815 (m), 1662 (s), 1633 (w) $cm^{-1}$. Infrared spectrum of the red powder (KBr disk): 2979 (m), 2937 (sh), 2894 (m), 1936 (sh), 1897 (s), 1830 (s), 1654 (s), 1485 (w), 1458 (w), 1346 (w), 1250 (w), 1185 (w), 1096 (w), 1020 (m), 919 (w), 867 (m), 646 (s), 567 (m), 521 (w), 480 (w) $cm^{-1}$. $^1H$ NMR spectrum in $CD_3CN$: three very large, broad, overlapping peaks centered at $\delta$ 2.43, 5.76, and 6.79, and three very small peaks at $\delta$ −0.32, 0.49, and 0.88. Analysis: Four samples in sealed ampules were sent to two analytical laboratories. The values obtained from these analyses varied over a wide range, and none of them indicated a stoichiometric loss of tetrahydrofuran. The samples were made up of initially crystalline, homogeneous material, and the failure to obtain reproducible analyses is presumably due to variable loss of tetrahydrofuran and the extreme sensitivity of the compound to oxygen. Solubility: $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ is soluble in diethyl ether, tetrahydrofuran, dichloromethane, and acetonitrile. It is insoluble in hexane.

**Preparation of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (1), $Mn_3(THF)_2(CO)_{10}$ (2), and $[Mn(THF)_6][Mn(CO)_5]_2$ (3).** $Mn_2(CO)_{10}$ (0.2930 g, 0.7513 mmol) was dissolved in a mixture of dry hexane (40 mL) and tetrahydrofuran (20 mL), and $Al(CH_3)_3$ (0.4 mL, 0.3 g, 4 mmol) was added with stirring. The mixture was then heated to reflux, stirred for 47 h, and then allowed to cool to 25 °C to form an orange solution and a red powder precipitate. The orange solution was transferred to another flask via cannula. The red powder was identified as $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (1) by its infrared spectrum in THF solution. The volume of the orange solution was reduced to 20 mL under vacuum, and the solution was then cooled to −20 °C. After 24 h a yellow powder precipitated, and the orange mother liquor was transferred via cannula to another flask. The yellow powder was redissolved in THF (10 mL) and the resulting solution was cooled to −20 °C to produce a mixture of yellow parallelepipeds ($Mn_3(THF)_2(CO)_{10}$ (2)) and yellow needle crystals ($[Mn(THF)_6][Mn(CO)_5]_2$ (3)). The identities of both compounds were established by single-crystal X-ray diffraction. Both compounds rapidly lose tetrahydrofuran, and all attempts to isolate them by fractional crystallization resulted in decomposition to form $Mn_2(CO)_{10}$, which is observed in all solutions of these compounds throughout the reaction and the workup procedure. The infrared spectrum of the yellow powder exhibits the following absorptions ($\nu_{CO}$, THF solution): 2062 (w), 2045 (m), 2009 (m), 1951 (s), 1931 (s), 1900 (m), 1866 (m), 1850 (sh), 1735 (w) $cm^{-1}$. When hexane was added to the yellow powder to give a yellow solution and insoluble yellow powder, the infrared spectrum of the solution showed the following absorptions: 2045 (m), 2014 (s), 1983 (m) $cm^{-1}$. The infrared spectrum[11] ($\nu_{CO}$, cyclohexane solution) of $Mn_2(CO)_{10}$ has been reported in the literature: 2044 (m), 2013 (vs), 2001 (w), 1993 (vw), 1983 (m), 1956 (vw), 1949 (vw) $cm^{-1}$. Likewise, the reported spectrum[12] ($\nu_{CO}$, THF solution) for the $Mn(CO)_5^-$ anion is 1896 (s), 1862 (s), 1830 (m) $cm^{-1}$. Repeated attempts to isolate compounds **2** and **3** led only to the formation of $Mn_2(CO)_{10}$. We have tentatively assigned the absorptions at 2062, 1951, and 1931 $cm^{-1}$ in the infrared spectrum of the yellow powder in THF as belonging to $Mn_3(THF)_2(CO)_{10}$.

In other similar preparations the same initial procedure was followed, but after the reaction mixture was heated to reflux and then allowed to cool to 25 °C the solution was allowed to stand undisturbed at this temperature for periods of 12 h or longer. This produced large black crystals of $[Mn][Mn_7(THF)_6(CO)_{12}]_2 \cdot 2Al(CH_3)_3(THF)$, which gave the same infrared spectrum as the aluminum-free $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ when dissolved in tetrahydrofuran, but the solid-state infrared spectrum in a KBr disk was quite different: 2963 (w), 2931 (w), 2878 (w), 2027 (s), 1904 (vs), 1578 (m), 1474 (m), 1388 (m), 1262 (w), 1099 (w), 1046 (w), 803 (w), 642 (m), 514 (w) $cm^{-1}$. Crystals containing the $Al(CH_3)_3(THF)$ complex are black and opaque, whereas the crystals that do not contain this species appear dark red and are more transparent. The two can be distinguished by their solid-state infrared spectra and their unit cell parameters.

**Crystal Structure Determinations.** Suitable crystals were sealed in thin-walled glass capillaries under a tetrahydrofuran-saturated atmosphere of dry nitrogen. Data collection was performed on a Siemens Model P4 automated diffractometer using Mo K$\alpha$ radiation. The unit cell parameters were determined and refined by a least-squares fit of 24 high-angle reflections. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on $\Psi$ scans were applied. The space group determinations were based upon a check of the Laue symmetry and systematic absences present and were confirmed by the structure solution. The structures were determined by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-Ray Instruments, Inc. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms unless otherwise specified. Hydrogen atoms were placed in calculated positions but were not refined. ORTEP[13] drawings are shown with 30% probability ellipsoids. Full details for the structure determinations are available in the supplementary material.

**$[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (1).** Although the complex crystallizes quite readily, many of the tetrahydrofuran molecules that accompany

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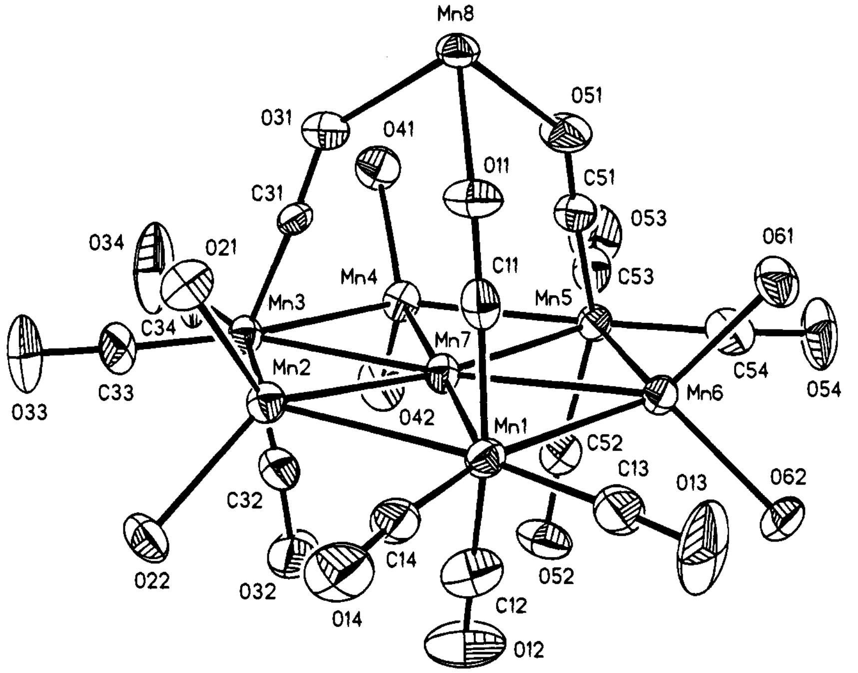

**Figure 1.** ORTEP drawing of half of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (1). Mn8 resides on a center of symmetry. Carbon atoms on the THF rings have been omitted for clarity.

it are easily lost, and this results in crystals of poor quality for X-ray diffraction studies. After examining many crystals and collecting data sets for three of them, we were able to obtain a structure that refined to an acceptable agreement factor. The crystal used for this study was obtained from the orange mother liquor that is produced in the hexane/THF mixed-solvent procedure used to prepare compounds **2** and **3**. This sample, which gave the best quality data set, contained one molecule of the $Al(CH_3)_3(THF)$ adduct per asymmetric unit. The $Al(CH_3)_3(THF)$ exhibited some rotational disorder about the Al−O axis, and hence there are several residual peaks near the methyl groups and the tetrahydrofuran ring, which is poorly resolved. The four carbon atoms in this THF were refined isotropically, and hydrogen atom positions were not calculated for the $Al(CH_3)_3(THF)$ adduct.

Another structure determination was performed for a crystal that did not contain $Al(CH_3)_3(THF)$. This crystal was obtained from the high-yield preparation that employed pure tetrahydrofuran rather than the THF/hexane mixed solvent, and although it gave a much weaker data set, the quality of the data was sufficient to determine that the structure of the $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ complex was virtually the same as that found in the crystal of $[Mn][Mn_7(THF)_6(CO)_{12}]_2{\cdot}2Al(CH_3)_3(THF)$. Crystal data: monoclinic space group $P2_1/c$ (No. 14), a = 18.268(2) Å, b = 20.395(4) Å, c = 15.143(2) Å, $\beta$ = 103.064(8)°, Z = 2, $R$ = 8.75%, $R_w$ = 9.55%.

**$Mn_3(THF)_2(CO)_{10}$ (2).** The structure was determined routinely in the manner described above.

**$[Mn(THF)_6][Mn(CO)_5]_2$ (3).** Crystals of this compound are highly unstable at room temperature with respect to loss of tetrahydrofuran. After many attempts, a sample was successfully mounted in a sealed glass capillary under a THF-saturated atmosphere of dry nitrogen. The structure determination revealed that the manganese atoms of the $Mn(THF)_6^{2+}$ ions reside on centers of symmetry at 0, 0, 0 and 0.5, 0.5, 0.5 so that there are two $Mn(CO)_5^-$ ions and two halves of a $Mn(THF)_6^{2+}$ ion in the asymmetric unit. The THF rings attached to Mn(4) exhibited a small amount of disorder such that alternate positions could be observed for the carbon atoms attached to the oxygens. The site occupancy factors for the carbons in these rings were refined (one factor for all four carbons of each ring) to give values ranging from 84% to 91%. The alternate positions (two carbons for each THF) were refined isotropically with site occupancy factors such that for each carbon the factors for both positions summed to unity.

## Results and Discussion

**$[Mn][Mn_7(THF)_6(CO)_{12}]_2{\cdot}2Al(CH_3)_3(THF)$.** The crystal structure of $[Mn][Mn_7(THF)_6(CO)_{12}]_2{\cdot}2Al(CH_3)_3(THF)$ (Figures 1 and 2) consists of two $Mn_7(THF)_6(CO)_{12}$ units, each of which is coordinated to an isolated manganese atom (Mn8) via three carbonyl oxygens to give an octahedral coordination geometry about this atom. The isolated manganese resides on a crystallographic center of symmetry. The framework of each $Mn_7(THF)_6(CO)_{12}$ unit consists of a ring of six manganese atoms, all of which are attached to a seventh manganese in the center of the ring to form a planar $Mn_7$ unit. The coordination

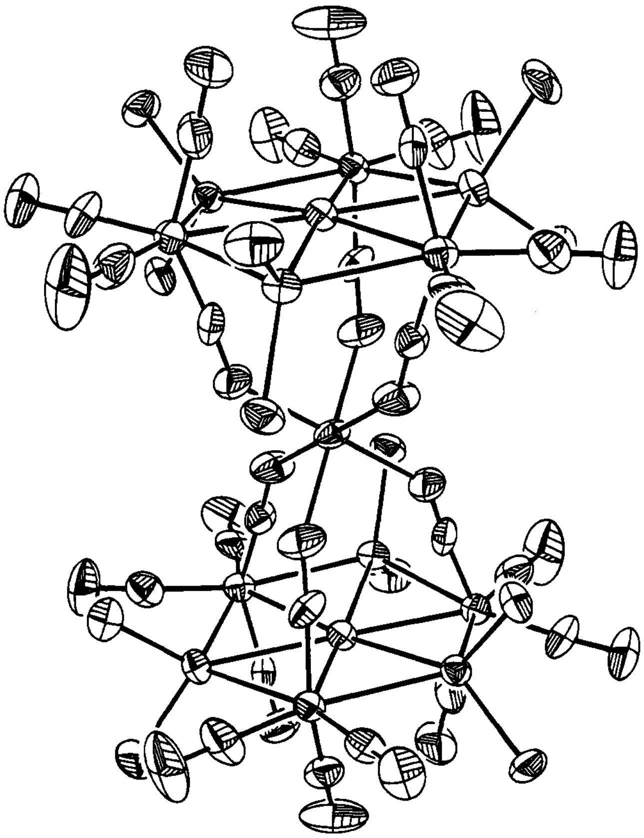

**Figure 2.** ORTEP drawing of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (1). Carbon atoms on the THF rings have been omitted for clarity.

**Table 1.** Crystallographic Data for $[Mn][Mn_7(THF)_6(CO)_{12}]_2{\cdot}2Al(CH_3)_3THF$ (**1**), $Mn_3(THF)_2(CO)_{10}$ (**2**), and $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**)

| | **1** | **2** | **3** |
|---|---|---|---|
| chemical formula | $C_{96}H_{130}Al_2Mn_{15}O_{38}$ | $C_{18}H_{16}Mn_3O_{12}$ | $C_{34}H_{48}Mn_3O_{16}$ |
| formula weight | 2770.06 | 589.14 | 877.57 |
| crystal system | monoclinic | monoclinic | triclinic |
| space group | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) |
| $a$, Å | 13.630(3) | 8.9394(7) | 10.352(1) |
| $b$, Å | 24.847(5) | 16.795(2) | 10.443(1) |
| $c$, Å | 17.645(4) | 16.048(2) | 19.552(3) |
| α, deg | | | 83.86(1) |
| $\beta$, deg | 106.01(3) | 95.239(8) | 88.14(1) |
| $\gamma$, deg | | | 86.037(9) |
| volume, Å$^3$ | 5744(2) | 2399.3(5) | 2095.8(6) |
| $Z$ | 2 | 4 | 2 |
| $\varrho$(calc), g cm$^{-3}$ | 1.602 | 1.631 | 1.391 |
| $\mu$(Mo Kα), cm$^{-1}$ | 16.8 | 16.12 | 9.5 |
| temp, K | 296 | 296 | 296 |
| no. of ind. reflcns | 7768 | 3356 | 5819 |
| no. of obs reflcns ($F > 4.0\,\sigma(F)$) | 3047 | 1777 | 3566 |
| transmission coeff. | 0.59−0.82 | 0.85−0.95 | 0.87−0.94 |
| no. of parameters | 617 | 298 | 508 |
| $R^a$ (obs data) | 0.0656 | 0.0426 | 0.0657 |
| $R_w{}^b$ (obs data) | 0.0675 | 0.0385 | 0.0907 |
| goodness of fit | 1.32 | 1.35 | 1.38 |

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

environment of the central manganese is exceedingly rare for a transition metal, and to our knowledge has only been observed for a copper atom in $[Et_4N]_3\ [Cu_5Fe_4(CO)_{16}]$,[14] a silver atom in $[Et_4N]_3\ [Ag_5\{\mu_2\text{-}Fe(CO)_4\}_2\{\mu_3\text{-}Fe(CO)_4\}_2]$,[15] and a nickel that is coordinated to six phosphorus atoms in the complex $Ni\{PC(CH_3)_3\}_6$.[16] A related species, the $[In\{Mn(CO)_4\}_5]^{2-}$ anion, has recently been reported in which the indium is coordinated to five manganese atoms in an approximate pentagonal planar arrangement.[8] The six-membered ring of the $Mn_7(THF)_6(CO)_{12}$ unit is made up of alternating $Mn(CO)_4$ and $Mn(THF)_2$ groups, and if metal−metal bonds to the central manganese are ignored, the former have approximate octahedral coordination while the latter have somewhat distorted tetrahedral geometries.

The most striking feature of the structure is the central metal of the $Mn_7$ moiety. The distances from this atom (Mn7) to the three $Mn(CO)_4$ metals average 2.651(4) Å, and the average distance to the three $Mn(THF)_2$ metals is 2.785(4) Å. The six $Mn(CO)_4$−$Mn(THF)_2$ metal−metal distances fall between these two values, with an average length of 2.722(4) Å. Although these numbers are within the range of distances for normal covalent Mn−Mn bonds,[17] they are among the shortest distances yet observed and are considerably less than the more typical Mn−Mn distance of 2.923 Å observed for dimanganese decacarbonyl.[18] The $Mn_7$ framework is virtually planar, with a mean distance of 0.087(4) Å from the metals to the mean least−squares plane through them. The greatest deviation from the plane is 0.148(4) Å, and the central manganese shows a deviation of 0.086(4) Å. The three carbonyl groups above the plane that are coordinated to the isolated manganese (Mn8) and the three carbonyls below the $Mn_7$ plane lean inward toward the central manganese (Mn7) with $Mn_{(center)}$−$Mn_{(ring)}$−C angles that average 71.6(6)°, which is substantially less than an idealized angle of 90°. There is essentially no distinction between the two types of carbonyls with regard to this parameter. This structural feature was also observed for $[Et_4N]_3[Cu_5Fe_4(CO)_{16}]$, which has $Cu_{(center)}$−$Fe_{(ring)}$−C angles of 68.8°,[14] and may be the result of steric repulsions from the other ligands that tip these carbonyls toward the relatively uncongested area in the center of the ring. It is interesting to note, however, that this distortion is not observed in other related transition metal rings.[9,19] The cluster complex $Mn_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2$, which has $Mn(CO)_4$ units attached to a trigonal planar gallium, has similar steric environments for the axial carbonyl groups but does not exhibit this type of distortion toward the gallium.[20] It is therefore possible that the coordinative and electronic unsaturation of the central manganese gives rise to electronic interactions between this atom and the carbonyls on adjacent metals. The average distance between the central manganese and the six carbonyl carbons is 2.69(2) Å and the average distance to the oxygens is 3.35(3) Å. These Mn−C and Mn−O values are well outside the range commonly observed for both side-on coordinated carbonyls, as typified by Mn−C and Mn−O distances of 2.01(3) and 2.29(2) Å in $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$,[21] and semibridging carbonyls, as represented by the Fe-C distances of 2.221(7) and 2.246(9) Å for these ligands in $(diars)Fe_3(CO)_{10}$ (diars = *o*-phenylenebis(dimethylarsine)).[22] It therefore appears that while there may be a very weak bonding interaction between the central manganese and the axial carbonyl carbons in the solid state, this metal is essentially bound only to the six manganese atoms of the ring.

Other intriguing features of the complex are the manganese atoms coordinated to the tetrahydrofurans. Although there are a few examples of transition metal compounds in which THF acts as a ligand,[23] these generally fall into one of two classifications: the metal either has substantial cationic character or is attached to $\pi$-acid ligands such as carbon monoxide that can remove electron density from the metal. The manganese atoms in the six-membered ring are attached only to the electron-donating tetrahydrofurans, which have no $\pi$-acid capabilities, and other metals. The average of the six Mn−O distances is 2.135(17) Å, which is quite close to the value of 2.100(4) Å observed for $[Mn(CO)_3(THF)(\mu\text{-}Cl)]_2$.[23a] As in most metal complexes of tetrahydrofuran, the oxygen atoms have nearly trigonal planar geometries, with angles that sum to an average of 358.3(25)°.

The two $Mn_7(THF)_6(CO)_{12}$ groups are coordinated to the isolated manganese of the complex (Mn8) via three carbonyl ligands from each group to form six "isocarbonyl" attachments that give the metal very close to octahedral geometry. The Mn−O distances average 2.147(15) Å and the Mn−O−C angles average 141.5(12)°. Isocarbonyl linkages have frequently been observed when electropositive metals such as the lanthanides,[24] early transition metals,[25] or alkali metals[26] are combined with

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**Table 2.** Selected Bond Distances (Å) and Angles (deg) for $[Mn][Mn_7(THF)_6(CO)_{12}]_2{\cdot}2Al(CH_3)_3THF$ (**1**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mn(1)–Mn(2) | 2.698(3) | Mn(1)–Mn(6) | 2.727(4) | Mn(4)–O(42) | 2.155(17) | Mn(5)–Mn(6) | 2.740(4) |
| Mn(1)–Mn(7) | 2.639(3) | Mn(1)–C(11) | 1.772(21) | Mn(5)–Mn(7) | 2.662(4) | Mn(5)–C(51) | 1.756(20) |
| Mn(1)–C(12) | 1.800(24) | Mn(1)–C(13) | 1.787(20) | Mn(5)–C(52) | 1.801(20) | Mn(5)–C(53) | 1.798(21) |
| Mn(1)–C(14) | 1.769(20) | Mn(2)–Mn(3) | 2.713(4) | Mn(5)–C(54) | 1.784(23) | Mn(6)–Mn(7) | 2.800(4) |
| Mn(2)–Mn(7) | 2.784(4) | Mn(2)–O(21) | 2.170(14) | Mn(6)–O(61) | 2.136(13) | Mn(6)–O(62) | 2.117(14) |
| Mn(2)–O(22) | 2.117(12) | Mn(3)–Mn(4) | 2.717(4) | Mn(8)–O(11) | 2.145(11) | Mn(8)–O(31) | 2.156(13) |
| Mn(3)–Mn(7) | 2.652(3) | Mn(3)–C(31) | 1.722(18) | Mn(8)–O(51) | 2.141(15) | Al–C(1) | 2.000(23) |
| Mn(3)–C(32) | 1.824(22) | Mn(3)–C(33) | 1.735(20) | Al–C(2) | 1.993(30) | Al–C(3) | 1.957(38) |
| Mn(3)–C(34) | 1.782(20) | Mn(4)–Mn(5) | 2.737(4) | Al–O(1) | 1.831(21) | | |
| Mn(4)–Mn(7) | 2.770(4) | Mn(4)–O(41) | 2.116(13) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mn(2)–Mn(1)–Mn(6) | 124.8(1) | Mn(2)–Mn(1)–C(11) | 75.4(5) | Mn(7)–Mn(5)–C(52) | 71.8(6) | C(51)–Mn(5)–C(52) | 144.1(8) |
| Mn(6)–Mn(1)–C(11) | 78.0(6) | Mn(7)–Mn(1)–C(11) | 70.7(5) | Mn(4)–Mn(5)–C(53) | 71.5(6) | Mn(6)–Mn(5)–C(53) | 163.8(6) |
| Mn(2)–Mn(1)–C(12) | 88.5(7) | Mn(6)–Mn(1)–C(12) | 85.1(7) | Mn(7)–Mn(5)–C(53) | 133.1(7) | C(51)–Mn(5)–C(53) | 102.6(9) |
| Mn(7)–Mn(1)–C(12) | 72.6(6) | C(11)–Mn(1)–C(12) | 143.3(8) | C(52)–Mn(5)–C(53) | 104.6(9) | Mn(4)–Mn(5)–C(54) | 160.5(7) |
| Mn(2)–Mn(1)–C(13) | 163.0(7) | Mn(6)–Mn(1)–C(13) | 71.9(7) | Mn(6)–Mn(5)–C(54) | 75.0(6) | Mn(7)–Mn(5)–C(54) | 137.1(6) |
| Mn(7)–Mn(1)–C(13) | 134.1(7) | C(11)–Mn(1)–C(13) | 108.2(8) | C(51)–Mn(5)–C(54) | 102.9(9) | C(52)–Mn(5)–C(54) | 100.2(9) |
| C(12)–Mn(1)–C(13) | 96.9(10) | Mn(2)–Mn(1)–C(14) | 71.8(6) | C(53)–Mn(5)–C(54) | 89.8(9) | Mn(1)–Mn(6)–Mn(5) | 114.4(1) |
| Mn(6)–Mn(1)–C(14) | 163.4(6) | Mn(7)–Mn(1)–C(14) | 133.5(6) | Mn(1)–Mn(6)–O(61) | 110.9(4) | Mn(5)–Mn(6)–O(61) | 112.6(4) |
| C(11)–Mn(1)–C(14) | 108.0(9) | C(12)–Mn(1)–C(14) | 97.4(9) | Mn(7)–Mn(6)–O(61) | 131.7(4) | Mn(1)–Mn(6)–O(62) | 113.1(4) |
| C(13)–Mn(1)–C(14) | 91.5(9) | Mn(1)–Mn(2)–Mn(3) | 115.1(1) | Mn(5)–Mn(6)–O(62) | 112.0(4) | Mn(7)–Mn(6)–O(62) | 136.5(4) |
| Mn(1)–Mn(2)–O(21) | 109.3(3) | Mn(3)–Mn(2)–O(21) | 114.9(3) | O(61)–Mn(6)–O(62) | 91.8(5) | Mn(1)–Mn(7)–Mn(2) | 59.6(1) |
| Mn(7)–Mn(2)–O(21) | 131.1(3) | Mn(1)–Mn(2)–O(22) | 112.6(3) | Mn(2)–Mn(7)–Mn(3) | 59.8(1) | Mn(3)–Mn(7)–Mn(4) | 60.1(1) |
| Mn(3)–Mn(2)–O(22) | 109.9(4) | Mn(7)–Mn(2)–O(22) | 135.9(4) | Mn(4)–Mn(7)–Mn(5) | 60.5(1) | Mn(1)–Mn(7)–Mn(6) | 60.1(1) |
| O(21)–Mn(2)–O(22) | 93.0(5) | Mn(2)–Mn(3)–Mn(4) | 124.5(1) | Mn(5)–Mn(7)–Mn(6) | 60.2(1) | O(11)–Mn(8)–O(31) | 89.9(5) |
| Mn(2)–Mn(3)–C(31) | 79.9(5) | Mn(4)–Mn(3)–C(31) | 80.6(6) | O(11)–Mn(8)–O(51) | 87.5(5) | O(31)–Mn(8)–O(51) | 88.5(5) |
| Mn(7)–Mn(3)–C(31) | 71.5(6) | Mn(2)–Mn(3)–C(32) | 84.6(6) | Mn(8)–O(11)–C(11) | 142.3(12) | Mn(8)–O(31)–C(31) | 140.9(11) |
| Mn(4)–Mn(3)–C(32) | 81.0(6) | Mn(7)–Mn(3)–C(32) | 71.5(6) | Mn(8)–O(51)–C(51) | 141.3(12) | Mn(2)–O(21)–C(21) | 124.1(12) |
| C(31)–Mn(3)–C(32) | 143.0(8) | Mn(2)–Mn(3)–C(33) | 71.7(6) | Mn(2)–O(21)–C(24) | 126.6(11) | C(21)–O(21)–C(24) | 107.3(15) |
| Mn(4)–Mn(3)–C(33) | 163.8(6) | Mn(7)–Mn(3)–C(33) | 134.0(6) | Mn(2)–O(22)–C(25) | 128.2(15) | Mn(2)–O(22)–C(28) | 129.2(15) |
| C(31)–Mn(3)–C(33) | 104.7(9) | C(32)–Mn(3)–C(33) | 101.9(9) | C(25)–O(22)–C(28) | 101.7(19) | Mn(4)–O(41)–C(41) | 124.0(18) |
| Mn(2)–Mn(3)–C(34) | 161.9(7) | Mn(4)–Mn(3)–C(34) | 73.5(7) | Mn(4)–O(41)–C(44) | 136.3(19) | C(41)–O(41)–C(44) | 99.4(24) |
| Mn(7)–Mn(3)–C(34) | 135.6(7) | C(31)–Mn(3)–C(34) | 103.7(9) | Mn(4)–O(42)–C(45) | 125.3(16) | Mn(4)–O(42)–C(48) | 131.1(19) |
| C(32)–Mn(3)–C(34) | 101.4(11) | C(33)–Mn(3)–C(34) | 90.3(9) | C(45)–O(42)–C(48) | 98.9(25) | Mn(6)–O(61)–C(61) | 126.6(16) |
| Mn(3)–Mn(4)–Mn(5) | 115.4(1) | Mn(3)–Mn(4)–O(41) | 109.7(4) | Mn(6)–O(61)–C(64) | 130.0(13) | C(61)–O(61)–C(64) | 102.3(19) |
| Mn(5)–Mn(4)–O(41) | 113.3(4) | Mn(7)–Mn(4)–O(41) | 138.0(5) | Mn(6)–O(62)–C(65) | 128.5(18) | Mn(6)–O(62)–C(68) | 127.8(14) |
| Mn(3)–Mn(4)–O(42) | 111.4(4) | Mn(5)–Mn(4)–O(42) | 111.1(4) | C(65)–O(62)–C(68) | 102.6(20) | Mn(1)–C(11)–O(11) | 175.5(15) |
| Mn(7)–Mn(4)–O(42) | 127.9(4) | O(41)–Mn(4)–O(42) | 94.1(6) | Mn(3)–C(31)–O(31) | 175.2(15) | Mn(5)–C(51)–O(51) | 176.6(14) |
| Mn(4)–Mn(5)–Mn(6) | 124.1(1) | Mn(4)–Mn(5)–C(51) | 86.9(6) | C(1)–Al–C(2) | 115.8(12) | C(1)–Al–C(3) | 113.1(13) |
| Mn(6)–Mn(5)–C(51) | 76.2(5) | Mn(7)–Mn(5)–C(51) | 72.6(5) | C(2)–Al–C(3) | 115.5(12) | C(1)–Al–O(1) | 101.8(12) |
| Mn(4)–Mn(5)–C(52) | 80.0(6) | Mn(6)–Mn(5)–C(52) | 83.8(5) | C(2)–Al–O(1) | 105.5(11) | C(3)–Al–O(1) | 102.7(13) |

late transition metal complexes, but this type of coordination is rare for manganese.

The crystal lattice contained one molecule of the $Al(CH_3)_3(THF)$ adduct per asymmetric unit. Although a number of structure determinations have been performed for ether adducts of organoaluminum compounds in general and of trimethylaluminum in particular,[27] to our knowledge the $Al(CH_3)_3(THF)$ adduct has been structurally characterized in only one other compound in which it acts as a bridging group between two $Ca(\eta^5\text{-}Me_5C_5)_2$ moieties.[28] The bond distances and angles in $Al(CH_3)_3(THF)$ are similar to those observed in the other compounds, with the exception of the Al–O distance of 1.831(21) Å, which falls considerably outside the range of 1.9–2.0 Å that is typical of the other known complexes. This result should not be accorded a great deal of significance in light of the fact that the adduct was poorly resolved in the structure determination, as described in the Experimental Section.

The solid-state infrared spectrum of crystalline $[Mn][Mn_7(THF)_6(CO)_{12}]_2{\cdot}2Al(CH_3)_3(THF)$ in a KBr disk exhibits a strong sharp absorption at 2029 $cm^{-1}$ and a strong broad peak at 1911 $cm^{-1}$, with two additional broad peaks at 1475 and 1388 $cm^{-1}$. These two pairs of peaks are consistent with the expected spectrum for *fac*-$L_3M(CO)_3$ and *fac*-$L_3M(OC)_3$ metal centers.[29] The complex $Cp_2ZrMe(\mu\text{-}OC)Cr(CO)_2Cp$, in which the zirconium is coordinated to a carbonyl oxygen, exhibits a strong broad absorption at 1540 $cm^{-1}$ in Nujol mull for the C–O stretching mode of the isocarbonyl ligand.[25] Coordination of the more strongly electron-withdrawing $Mn^{2+}$ cation to the carbonyls in $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (**1**) presumably shifts the isocarbonyl absorptions to lower frequency. The infrared spectrum of pure tetrahydrofuran shows absorptions at 1460 and 1370 $cm^{-1}$; however, these are overshadowed by much stronger peaks at 2900, 1070, and 910 $cm^{-1}$. These three strong peaks show up only as very weak absorptions in the solid-state spectrum of **1**, so the moderately strong absorptions at 1475 and 1388 $cm^{-1}$ are most likely due to the isocarbonyls. The spectrum of the complex in tetrahydrofuran solution is dramatically different from that observed in the solid state. It is consistent with a process in which the complex dissociates into a $Mn^{2+}$ cation and two $Mn_7(THF)_6(CO)_{12}^-$ anions, and one or more of the carbonyl ligands adopt side-on coordination. Dissociation into free ions would have the effect of making the $Mn_7(THF)_6(CO)_{12}$ groups more electron-rich, which would increase back-donation of electron density from the manganeses into the $\pi^*$ orbitals of the CO ligands, thereby lowering the C–O stretching frequency. The two strong bands at 1899 and 1840 $cm^{-1}$ in the solution spectrum are greatly shifted to lower

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frequency relative to those in the solid-state spectrum. There are two additional weak absorptions at 1933 and 1815 cm$^{-1}$, and a new strong peak at 1662 cm$^{-1}$. The latter is in the appropriate region for a side-on bound carbonyl, and can be compared to the peak observed at 1645 cm$^{-1}$ for this ligand in $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$.[21] The absorptions at 1475 and 1388 cm$^{-1}$ in the solid-state spectrum that were assigned to the isocarbonyl groups are not present in the solution spectrum. Another possible explanation for the peak at 1662 cm$^{-1}$ is that the cluster undergoes extensive dissociation to form $Mn(CO)_4^{3-}$ anions, which exhibit absorptions at 1792 (w) and 1665 (vs, broad) cm$^{-1}$.[30]

One question that arises is whether or not there are any hydride ligands in the cluster. Hydrogen-bridged metal−metal bonds are generally longer than unbridged bonds,[31] although it is possible to find examples in which a hydrogen-bridged bond in one molecule is shorter than an unbridged bond in another. The longest Mn−Mn bond in the title complex is 2.800(4) Å (between Mn6 and Mn7). A survey of the Cambridge Crystallographic Database[32] revealed that out of 25 reported structures containing hydrogen-bridged Mn−Mn bonds, all but four have Mn−Mn distances greater than 2.84 Å. Of these four, $Mn_2(\mu\text{-}H)_2(\mu\text{-dppm})(CO)_6$ (dppm = $Ph_2PCH_2PPh_2$) (Mn−Mn = 2.699 Å)[33] and $Mn_2\{\mu\text{-}Ag(ClO_4)PPh_3\}(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})$ (Mn−Mn = 2.740 Å)[34] have two atoms bridging a formal Mn=Mn double bond. Of the other two, $Mn_2(\mu\text{-}H)(\mu\text{-}N{=}CHPh)(\mu\text{-dppm})(CO)_6$ (Mn−Mn = 2.818 Å)[35] has a bridging alkylidenimido group and $Mn_2\{\mu\text{-}C({=}O)C(Ph){=}CHPh\}(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6^-$ (Mn−Mn = 2.814 Å)[36] has both acyl and phosphido bridges in addition to the hydrogen atom bridge. The shortest hydrogen-bridged Mn−Mn bond that does not have another single-atom bridge is found in $HMn_3(CO)_{10}(BH_3)_2$ (Mn−Mn = 2.845(3) Å).[37] Representative distances for complexes in which a single hydride bridges an Mn−Mn bond are 2.881(3) Å for $HMn_3(CO)_{12}^{2-}$ [9] and 3.111(2) Å (average) for $H_3Mn_3(CO)_{12}$.[19] No significant residual electron density in a chemically reasonable position was observed at the conclusion of the structure determination, but this negative result cannot be regarded as conclusive in light of the mediocre quality of the data and the inherent difficulty of locating metal hydrides.[19] The $^1H$ NMR spectrum for the complex was examined in the region $\delta$ +95 to −85, and it showed only broad resonances between $\delta$ +7 and −0.5 that are typical for solutions containing paramagnetic species. The lack of resonances in the metal hydride region (negative $\delta$) suggests that these ligands are not present, but again this evidence is not conclusive because of the possibility that a metal hydride resonance could be greatly shifted as a result of the presence of paramagnetic species. There are no absorptions in the solid−state infrared spectrum in the region 2300−1600 cm$^{-1}$ that would suggest the presence of a metal hydride, although the solution spectrum shows weak absorbances at 1971, 1933, and 1815 cm$^{-1}$ that could be attributed to metal carbonyls or hydrides. We therefore conclude that we have no compelling physical evidence that indicates the presence of metal hydrides, although their existence cannot be completely ruled out.

We are currently conducting a number of studies to develop a comprehensive description of the metal−metal bonding in this complex; however, at this stage some qualitative features can be proposed. The solid-state structure of the cluster can be considered to be two $Mn_7(THF)_6(CO)_{12}^-$ anions coordinated to a $Mn^{2+}$ cation. The infrared spectrum of the complex in THF solution and the $^1H$ NMR spectrum in $CD_3CN$ are consistent with its dissolution to form these species, and the presence of a $Mn^{2+}$ ion is plausible in light of studies that suggest that dimanganese decacarbonyl in tetrahydrofuran can undergo disproportionation under photolytic conditions to form $Mn(THF)_6^{2+}$ and $Mn(CO)_5^-$ ions.[38] A very interesting discussion of the bonding in the related complexes $Ni\{PC(CH_3)_3\}_6$ and $[In\{Mn(CO)_4\}_5]^{2-}$ has appeared recently that pointed out the isolobal relationship between $SiH_2$, PR, and $Mn(CO)_4^-$ fragments.[39] A similar examination of the $Mn_7(THF)_6(CO)_{12}^-$ anion suggests that the orbital interaction scheme for this species may have qualitative similarities to that proposed for $Ni\{PC(CH_3)_3\}_6$. An alternative explanation involves viewing the cluster as being made up of intimately associated $Mn(CO)_4^{3-}$ anions and $Mn^{2+}$ cations. This is similar to the description proposed for the tetranuclear iron complex $[(py)_2FeFe(CO)_4]_2$ (py = pyridine), which reacts with ethylenediamine (en) to give $[Fe(en)_3][Fe(CO)_4]$, which is made up of separate $Fe(en)_3^{2+}$ cations and $Fe(CO)_4^{2-}$ anions.[40] The infrared spectrum of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ in THF solution shows a strong peak at 1662 cm$^{-1}$ that is very close in frequency to the peak at 1665 cm$^{-1}$ reported for the $Mn(CO)_4^{3-}$ anion,[30] so it is possible that the cluster may form these ions in solution. We are now in the midst of a series of studies to examine the reactivity of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (as well as its spectroscopic, electrochemical, and magnetic behavior) in an effort to better understand the metal−metal interactions in this unusual species.

**$Mn_3(THF)_2(CO)_{10}$ (2) and $[Mn(THF)_6][Mn(CO)_5]_2$ (3).** The reaction of dimanganese decacarbonyl with trimethylaluminum in a mixture of hexane and THF rather than in pure THF produced the unstable compounds $Mn_3(THF)_2(CO)_{10}$ (**2**) and $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**), in addition to $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ (**1**). The structure of **2** consists of two $Mn(CO)_5$ groups connected by metal−metal bonds to a central $Mn(THF)_2$ unit (Figure 3), and **3** consists of isolated $[Mn(THF)_6]^{2+}$ and $[Mn(CO)_5]^-$ ions (Figures 4 and 5). There are many similarities between the structure of $Mn_3(THF)_2(CO)_{10}$ and that of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$. The average Mn−Mn distance of 2.732(2) Å in **2** is close to the average Mn−Mn separation of 2.722(4) Å between the $Mn(THF)_2$ and $Mn(CO)_4$ groups in the $Mn_7$ cluster. Likewise, the average Mn−O distance of 2.148(5) Å in the $Mn(THF)_2$ group of **2** is virtually the same as the average value of 2.135(17) Å for the corresponding distances in **1**. Similarities between the two clusters also extend to $Mn_{(CO)}{-}Mn_{(THF)}{-}Mn_{(CO)}$ and O−Mn−O angles in the $Mn(THF)_2$ groups. It is interesting to note that $Mn_3(THF)_2(CO)_{10}$, as formulated, has an odd number of electrons and therefore must be paramagnetic. The instability of the complex has thus far prevented our investigation of its magnetic

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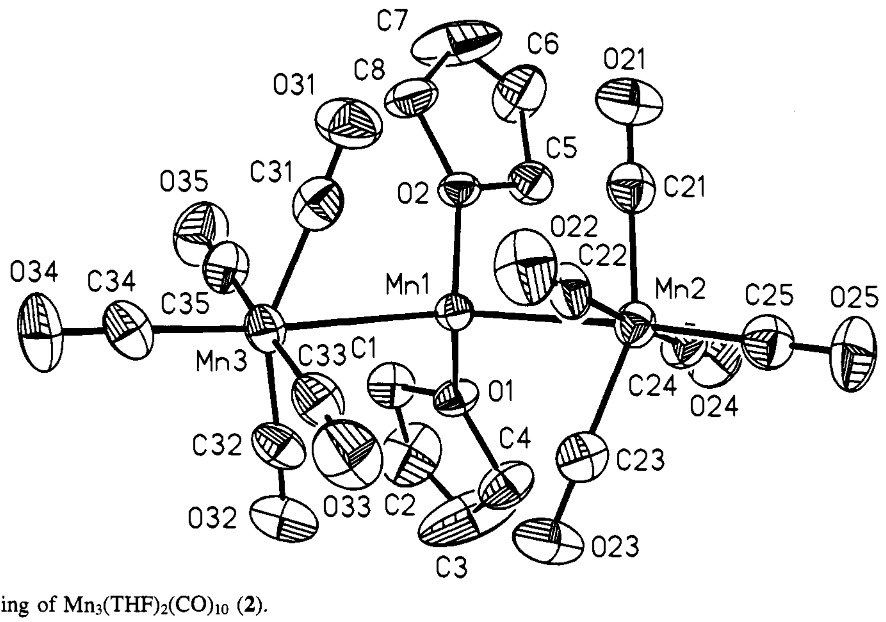

**Figure 3.** ORTEP drawing of $Mn_3(THF)_2(CO)_{10}$ (**2**).

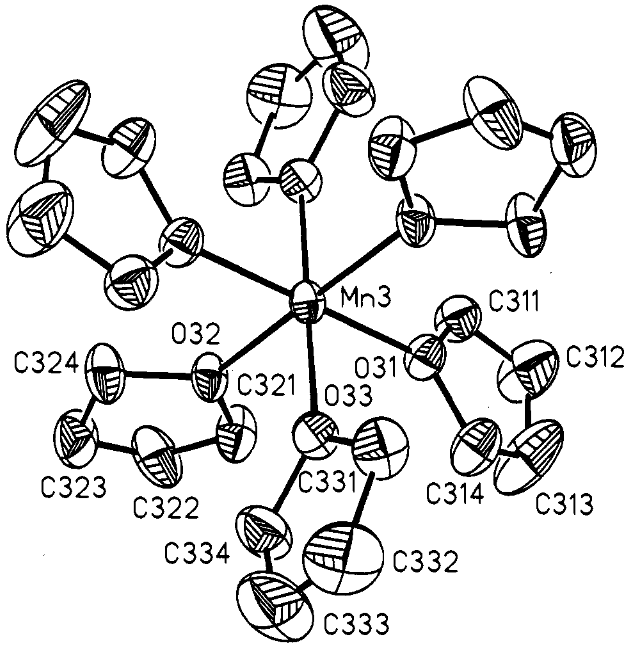

**Figure 4.** ORTEP drawing of one of the $Mn(THF)_6^{2+}$ cations of $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**). The manganese resides on a center of symmetry.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for $Mn_3(THF)_2(CO)_{10}$ (**2**)

| | | | |
|---|---|---|---|
| Mn(1)−Mn(2) | 2.725(2) | Mn(1)−Mn(3) | 2.738(2) |
| Mn(1)−O(1) | 2.152(5) | Mn(1)−O(2) | 2.144(5) |
| Mn(2)−C(21) | 1.800(8) | Mn(2)−C(22) | 1.835(9) |
| Mn(2)−C(23) | 1.820(9) | Mn(2)−C(24) | 1.814(9) |
| Mn(2)−C(25) | 1.836(9) | Mn(3)−C(31) | 1.834(9) |
| Mn(3)−C(32) | 1.796(9) | Mn(3)−C(33) | 1.811(10) |
| Mn(3)−C(34) | 1.818(9) | Mn(3)−C(35) | 1.816(10) |
| | | | |
| Mn(2)−Mn(1)−Mn(3) | 122.0(1) | Mn(2)−Mn(1)−O(1) | 113.0(1) |
| Mn(3)−Mn(1)−O(1) | 109.1(1) | Mn(2)−Mn(1)−O(2) | 109.3(1) |
| Mn(3)−Mn(1)−O(2) | 110.8(1) | O(1)−Mn(1)−O(2) | 87.1(2) |
| Mn(1)−Mn(2)−C(21) | 80.2(3) | Mn(1)−Mn(2)−C(22) | 89.3(3) |
| C(21)−Mn(2)−C(22) | 86.4(4) | Mn(1)−Mn(2)−C(23) | 74.3(3) |
| C(21)−Mn(2)−C(23) | 154.4(4) | C(22)−Mn(2)−C(23) | 90.8(4) |
| Mn(1)−Mn(2)−C(24) | 85.3(3) | C(21)−Mn(2)−C(24) | 89.3(4) |
| C(22)−Mn(2)−C(24) | 173.7(4) | C(23)−Mn(2)−C(24) | 91.0(4) |
| Mn(1)−Mn(2)−C(25) | 176.7(3) | C(21)−Mn(2)−C(25) | 102.9(4) |
| C(22)−Mn(2)−C(25) | 91.8(4) | C(23)−Mn(2)−C(25) | 102.6(4) |
| C(24)−Mn(2)−C(25) | 93.7(4) | Mn(1)−Mn(3)−C(31) | 73.9(3) |
| Mn(1)−Mn(3)−C(32) | 78.4(3) | C(31)−Mn(3)−C(32) | 152.1(4) |
| Mn(1)−Mn(3)−C(33) | 89.9(3) | C(31)−Mn(3)−C(33) | 89.8(4) |
| C(32)−Mn(3)−C(33) | 87.0(4) | Mn(1)−Mn(3)−C(34) | 175.8(3) |
| C(31)−Mn(3)−C(34) | 102.6(4) | C(32)−Mn(3)−C(34) | 105.2(4) |
| C(33)−Mn(3)−C(34) | 92.5(4) | Mn(1)−Mn(3)−C(35) | 85.7(3) |
| C(31)−Mn(3)−C(35) | 91.0(4) | C(32)−Mn(3)−C(35) | 90.1(4) |
| C(33)−Mn(3)−C(35) | 175.1(4) | C(34)−Mn(3)−C(35) | 92.1(4) |
| Mn(1)−O(1)−C(1) | 123.8(4) | Mn(1)−O(1)−C(4) | 126.0(5) |
| C(1)−O(1)−C(4) | 108.5(6) | Mn(1)−O(2)−C(5) | 121.9(4) |
| Mn(1)−O(2)−C(8) | 127.5(5) | C(5)−O(2)−C(8) | 108.8(6) |

and spectroscopic properties, and we are presently attempting to replace the tetrahydrofurans with other ligands that will stabilize the compound without disrupting the metal−metal bonds. As in the case of compound **1**, metal−metal bond lengths and the lack of significant electron density in a chemically reasonable position in the X-ray diffraction study suggest that there are no metal hydrides present, but this evidence cannot be taken as conclusive.

The structure of $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**) is entirely as expected. Both the octahedral $[Mn(THF)_6]^{2+}$ cation[23d] and the trigonal bipyramidal $[Mn(CO)_5]^-$ anion[41] have already been structurally characterized, both of them with other counterions, and the complex ions in **3** show minimal differences from these. It is interesting to compare the average Mn−O distances in the $[Mn(THF)_6]^{2+}$ cation (2.191(6) Å in **3** and 2.201(10) Å in $[Mn(THF)_6][I_3]_2$[23d]) to the values of 2.135(17) Å in **1** and 2.148(5) Å in **2**. The oxygen atoms have trigonal planar geometries in both the cations and the metal clusters.

**Formation of the Complexes.** Recent studies[38] have shown that under photolytic conditions dimanganese decacarbonyl in tetrahydrofuran can undergo disproportionation to form $Mn(THF)_6^{2+}$ and $Mn(CO)_5^-$ ions, and the isolation of substantial amounts of $[Mn(THF)_6][Mn(CO)_5]_2$ from the reaction of $Mn_2(CO)_{10}$ and $Al(CH_3)_3$ in a THF/hexane mixture makes it highly likely that the cluster complexes **1** and **2** are formed via stepwise combination of these ions. Conversion of $[Mn(THF)_6][Mn(CO)_5]_2$ to $Mn_3(THF)_2(CO)_{10}$ can occur as a result of electrostatic attraction between the ions and facile displacement of THF ligands from the coordination sphere of the cation. The detailed manner in which $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ is formed is not clear; however, the fact that the manganese atoms in this complex have either lost all carbonyls or retained four of the

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[41] Frenz, B. A.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 1109–1116.

**Table 4.** Selected Bond Distances (Å) and Angles (°) for $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mn(1)−C(11) | 1.754(12) | Mn(1)−C(12) | 1.750(13) | Mn(2)−C(24) | 1.777(14) | Mn(2)−C(25) | 1.792(12) |
| Mn(1)−C(13) | 1.762(13) | Mn(1)−C(14) | 1.819(13) | Mn(3)−O(31) | 2.196(5) | Mn(3)−O(32) | 2.184(5) |
| Mn(1)−C(15) | 1.589(16) | Mn(2)−C(21) | 1.825(13) | Mn(3)−O(33) | 2.192(5) | Mn(4)−O(41) | 2.199(5) |
| Mn(2)−C(22) | 1.819(11) | Mn(2)−C(23) | 1.712(12) | Mn(4)−O(42) | 2.194(5) | Mn(4)−O(43) | 2.181(6) |
| C(11)−Mn(1)−C(12) | 123.0(6) | C(11)−Mn(1)−C(13) | 87.1(6) | C(331)−O(33)−C(334) | 108.6(7) | Mn(4)−O(41)−C(411) | 127.8(6) |
| C(12)−Mn(1)−C(13) | 87.8(6) | C(11)−Mn(1)−C(14) | 119.0(6) | Mn(4)−O(41)−C(414) | 124.8(6) | C(411)−O(41)−C(414) | 107.4(8) |
| C(12)−Mn(1)−C(14) | 117.9(5) | C(13)−Mn(1)−C(14) | 91.0(6) | Mn(4)−O(41)−C(51) | 124.9(27) | C(411)−O(41)−C(51) | 63.8(28) |
| C(11)−Mn(1)−C(15) | 90.9(6) | C(12)−Mn(1)−C(15) | 91.7(8) | C(414)−O(41)−C(51) | 74.9(30) | Mn(4)−O(41)−C(54) | 126.6(28) |
| C(13)−Mn(1)−C(15) | 177.2(7) | C(14)−Mn(1)−C(15) | 91.7(7) | C(411)−O(41)−C(54) | 67.2(30) | C(414)−O(41)−C(54) | 73.1(31) |
| C(21)−Mn(2)−C(22) | 89.4(5) | C(21)−Mn(2)−C(23) | 123.4(6) | C(51)−O(41)−C(54) | 107.9(38) | Mn(4)−O(42)−C(421) | 126.0(6) |
| C(22)−Mn(2)−C(23) | 90.6(5) | C(21)−Mn(2)−C(24) | 121.2(6) | Mn(4)−O(42)−C(424) | 126.5(6) | C(421)−O(42)−C(424) | 107.5(7) |
| C(22)−Mn(2)−C(24) | 92.1(5) | C(23)−Mn(2)−C(24) | 115.4(6) | Mn(4)−O(42)−C(61) | 121.4(27) | C(421)−O(42)−C(61) | 71.4(28) |
| C(21)−Mn(2)−C(25) | 89.7(6) | C(22)−Mn(2)−C(25) | 176.3(6) | C(424)−O(42)−C(61) | 73.4(28) | Mn(4)−O(42)−C(64) | 130.8(49) |
| C(23)−Mn(2)−C(25) | 86.9(6) | C(24)−Mn(2)−C(25) | 91.4(6) | C(421)−O(42)−C(64) | 71.7(48) | C(424)−O(42)−C(64) | 62.1(46) |
| O(31)−Mn(3)−O(32) | 89.9(2) | O(31)−Mn(3)−O(33) | 90.7(2) | C(61)−O(42)−C(64) | 107.6(55) | Mn(4)−O(43)−C(431) | 127.4(6) |
| O(32)−Mn(3)−O(33) | 89.8(2) | O(41)−Mn(4)−O(42) | 90.0(2) | Mn(4)−O(43)−C(434) | 124.4(5) | C(431)−O(43)−C(434) | 108.1(8) |
| O(41)−Mn(4)−O(43) | 91.0(2) | O(42)−Mn(4)−O(43) | 90.5(2) | Mn(4)−O(43)−C(71) | 121.5(35) | C(431)−O(43)−C(71) | 61.3(33) |
| Mn(3)−O(31)−C(311) | 128.1(5) | Mn(3)−O(31)−C(314) | 125.1(5) | C(434)−O(43)−C(71) | 83.2(34) | Mn(4)−O(43)−C(74) | 122.6(66) |
| C(311)−O(31)−C(314) | 106.7(6) | Mn(3)−O(32)−C(321) | 125.7(5) | C(431)−O(43)−C(74) | 65.6(62) | C(434)−O(43)−C(74) | 77.0(61) |
| Mn(3)−O(32)−C(324) | 125.0(5) | C(321)−O(32)−C(324) | 109.3(6) | C(71)−O(43)−C(74) | 112.8(76) | | |
| Mn(3)−O(33)−C(331) | 125.4(5) | Mn(3)−O(33)−C(334) | 126.0(5) | | | | |

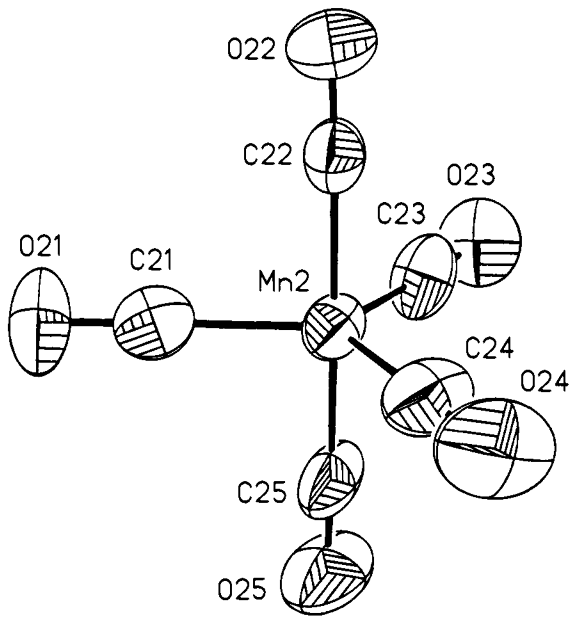

**Figure 5.** ORTEP drawing of one of the $Mn(CO)_5^-$ anions of $[Mn(THF)_6][Mn(CO)_5]_2$ (**3**).

original five carbonyl ligands suggests that it is also formed from $Mn(THF)_6^{2+}$ and $Mn(CO)_5^-$ ions. The role of the trimethylaluminum is not apparent at this time. Mechanistic studies are currently underway to obtain further information about the manner in which **1** is formed, with the object of developing a rational synthesis for new clusters of this type.

## Conclusions

The isolation of $[Mn][Mn_7(THF)_6(CO)_{12}]_2$ and $Mn_3(THF)_2(CO)_{10}$ offers a unique opportunity to study the behavior of metal atoms in very unusual molecular environments. Both compounds contain "lightly stabilized" manganese atoms coordinated solely to tetrahydrofuran and other metals. Other low-valent metal complexes such as $Ni(COD)_2$ (COD = 1,5-cyclooctadiene)[42] and $Pt(C_2H_4)_3$[43] that contain loosely coordinated ligands have exhibited a rich and varied reaction chemistry, and the electronically unsaturated manganese atoms in compounds **1** and **2** are expected to be highly reactive with respect to loss of THF and subsequent addition of other molecules. The central manganese of the $[Mn_7(THF)_6(CO)_{12}]^-$ anion is a very rare example of a transition metal having hexagonal planar coordination to six other metals, and as such it may provide insights into the behavior of atoms in bulk metal surfaces. Further studies of the reactivity and spectroscopic properties of these intriguing compounds are currently underway.

**Acknowledgment.** The authors gratefully acknowledge support from the Robert A. Welch Foundation through Grant No. D-1180 as well as from the Texas Higher Education Coordinating Board's Advanced Research Program Grant No. 3644180. The X-ray diffractometer was purchased with funds from Texas Tech University and the Texas Higher Education Coordinating Board's Energy Research in Applications Program Grant No. 3644-039. We also thank Professor Lawrence Dahl of the University of Wisconsin at Madison for helpful discussions.

**Supplementary Material Available:** Tables giving atomic positional parameters and anisotropic displacement coefficients for compounds **1**, **2**, and **3** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA942387+

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