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Xenophilic Metal Clusters: Preparation and Crystal Structure of $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ (THF = Tetrahydrofuran)

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In the field of transition metal cluster chemistry it is generally recognized that "the two general types of metal cluster compound, which may be loosely called the 'lower halide' type and the 'carbonyl' type, differ from each other in many ways, and there is very little in the way of chemical reactions to interrelate them."[1] The "lower halide" clusters are generally made up of cationic early transition metals in moderately low positive oxidation states that are bound to anionic ligands such as halides, alkoxides, or carboxylates that can act both as σ- and π-donors.[2] The "carbonyl" type contain later transition metals with zero or even negative oxidation states that are attached to π-acid ligands such as carbon monoxide, phosphines, or olefins.[3] We have recently prepared the manganese cluster complexes $[\text{Mn}][\text{Mn}_7(\text{THF})_6(\text{CO})_{12}]_2$ and $\{\mu\text{-Mn(THF)}_2\}[\text{Mn(CO)}_5]_2$ (THF = tetrahydrofuran),[4] which can be considered to have both types of metal centers in the same compound. These clusters are made up of manganese carbonyl fragments attached by metal−metal bonds to manganese atoms that are bound only to tetrahydrofuran donor ligands that have no π-acid capabilities. To our knowledge these are the only structurally-characterized compounds of this type in which all of the metals have open d-orbital subshells. Related compounds such as *trans*-$\text{Pt(py)}_2[\text{Mn(CO)}_5]_2$ and *trans*-$\text{Pt(py)}_2[\text{Co(CO)}_4]_2$ (py = pyridine) have been reported[5] that contain metal−metal bonds between atoms that are attached to carbonyl groups and atoms that are coordinated solely to pyridine ligands. However, unlike the homonuclear manganese clusters, all of the metals in these complexes are bound to ligands that can act as π-acids. Fachinetti and co-workers have recently reported two very intriguing species, $[(\text{py})_2\text{FeFe(CO)}_4]_2$[6] and $[(\text{OC})_4\text{CoCo(py)}_3][\text{Co(CO)}_4]$,[7] and reactions of these compounds indicated that they produce cationic metal−pyridine centers and metal carbonyl anions in solution. For this reason they were termed "homonuclear ion pair (HNIP)" clusters,[8] although a later paper indicated that the ion pair designation may not be entirely applicable in that there appeared to be very little charge separation between the metal centers in $[(\text{py})_2\text{FeFe(CO)}_4]_2$.[9]

We now wish to report the synthesis and crystallographic characterization of the paramagnetic complex $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ (**1**), a new member of this emerging third class of transition metal clusters. We propose the term "xenophilic" metal cluster for compounds of this general type (from the Greek "xenos", meaning foreigner or stranger, and "philos", meaning loving). This term emphasizes the fact that two very different types of metal centers are bonded together without implying that the interaction is purely ionic.

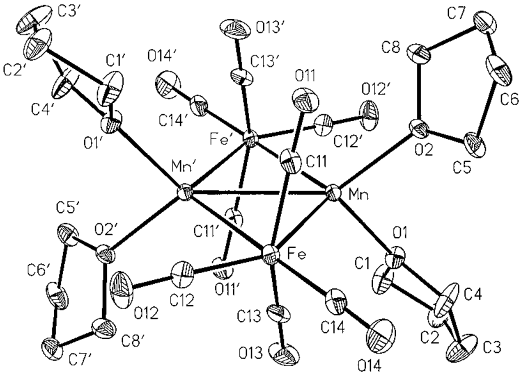

Figure 1. ORTEP drawing of $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ (**1**).

Compound **1** can be obtained quite readily from the reaction of $[\text{Mn}][\text{Mn}_7(\text{THF})_6(\text{CO})_{12}]_2$ with Fe(CO)_5 in tetrahydrofuran.[10] The crystal structure of **1** reveals that it is made up of two Fe(CO)_4 fragments connected by two Mn(THF)_2 bridges (Figure 1).[11] The molecule resides upon a crystallographic center of symmetry, which requires the Fe_2Mn_2 ring to be planar. The Fe−Mn distances of 2.633(1) and 2.601(1) Å are considerably

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[10] Fe(CO)_5 was purchased from the Aldrich Chemical Co. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or under argon in a drybox. Solvents were freshly distilled under an atmosphere of dry nitrogen from potassium (hexane) or sodium−potassium alloy (tetrahydrofuran). Fe(CO)_5 (1.0 mL, 1.5 g, 7.6 mmol) was added via syringe to a solution of $[\text{Mn}][\text{Mn}_7(\text{THF})_6(\text{CO})_{12}]_2$ (0.50 g, 0.21 mmol)[4] in dry tetrahydrofuran (40 mL), and the resulting mixture was heated at reflux for 19 h during which time the color remained dark red. The solution was cooled to 25 °C and all volatile materials were removed under vacuum to give a dark red solid that was then triturated with dry hexanes (50 mL). The hexane solution was removed via cannula and volatile materials were removed under vacuum to leave $\text{Mn}_2(\text{CO})_{10}$ (0.11 g, 0.28 mmol), which was identified by its infrared spectrum. The dark red solid was dissolved in THF (10 mL) and then cooled to −20 °C to give orange crystals of $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ (**1**). Yield: 0.24 g (34% based upon manganese). The compound decomposes immediately when exposed to air, either in solution or in the solid state. $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ is soluble in tetrahydrofuran and acetonitrile, and it is insoluble in hexane. Melting point: the compound decomposes above 155 °C. ^{1}H NMR spectrum in CD_3CN: two broad bands at δ 3.66 and 1.82, the latter of which was superimposed upon the CHD_2CN resonance at δ 1.93. These signals are assigned to the two types of methylene hydrogens in the THF ligands, which may or may not have been displaced from the manganese atoms by CD_3CN. No signal was observed in the ^{55}Mn NMR. Effective magnetic moment (μ_{eff}) = 5.0(1) μ_{B} at 25 °C. Infrared spectrum (ν_{CO}, THF solution): 1964 (s), 1898 (s), 1869 (s) cm^{-1}. Infrared spectrum (KBr disk): 2964 (w), 2902 (w), 2042 (w), 1958 (s), 1861 (s), 1262 (w), 1173 (vw), 1096 (w), 1019 (m), 921 (vw), 863 (w), 806 (w), 670 (w), 623 (s) cm^{-1}. Anal. Found: C, 39.14; H, 4.41; Fe, 14.61; Mn, 14.49 (Theory: C, 39.27; H, 4.39; Fe, 15.22; Mn, 14.97).

[11] Crystal data: $\text{C}_{24}\text{H}_{32}\text{Fe}_2\text{Mn}_2\text{O}_{12}$, M = 734.08, monoclinic, space group $P2_1/n$, a = 8.458(2) Å, b = 10.872(3) Å, c = 15.894(4) Å, β = 104.10(2)°, V = 1417.3(9) Å^3, D_c = 1.720 g cm^{-3}, Z = 2. A suitable crystal was coated with Paratone oil and then cooled to 173 K in an atmosphere of dry nitrogen. The structure was determined by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions but were not refined. After the hydrogen atoms were positioned and the refinement converged, separate least-squares refinements were carried out with different permutations of metal atom assignments. These refinements gave the following values for R: Fe(carbonyl) and Mn(THF) (R = 0.052, R_{m} = 0.067), all metals Mn (R = 0.053, R_{m} = 0.069), all metals Fe (R = 0.054, R_{m} = 0.070), Mn(carbonyl) and Fe(THF) (R = 0.056, R_{m} = 0.075). Although the individual differences between the R-factors in the alternate refinements have a very low statistical significance, we believe that the relative order of the four R factors is significant. All four R factors are in the order that is consistent with the proposed structure. Full details for the structure determination, including U(eq) values for the metal atoms in the alternative least-squares refinements, are available in the supporting information.

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Table 1. Selected Distances (Å) and Angles (deg) for $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ (**1**)

Fe−Mn	2.633(1)	Mn−C(13)	2.624(6)	Mn−O(1)	2.088(5)
Mn−Mn′	2.895(2)	Fe−Mn′	2.601(1)	Mn−C(11)	2.654(6)
Mn−O(2)	2.114(4)				

Mn−Fe−C(11)	71.3(2)	Mn−Fe−C(12)	144.5(2)
Mn−Fe−C(13)	70.3(2)	Mn−Fe−C(14)	112.0(2)
Mn−Fe−Mn′	67.2(1)	C(11)−Fe−Mn′	82.0(2)
C(12)−Fe−Mn′	77.3(2)	C(13)−Fe−Mn′	82.2(2)
C(14)−Fe−Mn′	179.2(2)	Fe−Mn−O(1)	112.9(1)
Fe−Mn−O(2)	111.4(1)	O(1)−Mn−O(2)	91.4(2)
Fe−Mn−Fe′	112.8(1)	O(1)−Mn−Fe′	111.4(1)
O(2)−Mn−Fe′	115.1(1)	Mn−O(1)−C(1)	126.6(4)
Mn−O(1)−C(4)	122.3(4)	C(1)−O(1)−C(4)	109.2(5)
Mn−O(2)−C(5)	123.8(3)	Mn−O(2)−C(8)	122.9(3)
C(5)−O(2)−C(8)	108.9(5)		

shorter than the average values of 2.813 Å found in $\text{FeMn}_2(\text{CO})_{14}$[12] and 2.841 Å in $(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{FeMn(CO)}_5$.[13] Of particular interest is the transannular Mn−Mn distance of 2.895(2) Å, which can be compared to the value of 2.923 Å observed for dimanganese decacarbonyl.[14] The Fe−Mn−Fe angle of 112.8(1)° is close to the ideal tetrahedral angle of 109.5°; however, the Mn−Fe−Mn angle of 67.2(1)° is substantially distorted from the ideal angle of 90° for octahedral coordination about iron. The carbonyl ligands that are above and below the Mn_2Fe_2 plane are considerably tilted toward the manganese atoms, with an average Mn−Fe−C angle of 70.8(2)° and Mn−C distances of 2.654 and 2.624 Å. The Mn−C values are well outside the range commonly observed for both side-on coordinated carbonyls, as typified by an Mn−C distance of 2.01(3) Å in $\text{Mn}_2(\text{CO})_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$,[15] and semibridging carbonyls, as represented by the Fe−C distances of 2.221(7) and 2.246(9) Å for these ligands in $(\text{diars})\text{Fe}_3(\text{CO})_{10}$ (diars = *o*-phenylenebis(dimethylarsine)).[16] There are no absorptions in the 1600−1800 cm^{-1} region of the solution and solid state infrared spectra of **1** that would be expected for side-on or semibridging carbonyls. It therefore appears that while there may be a very weak bonding interaction between each manganese and two of the axial carbonyl carbons in the solid state, these metals are essentially bound only to the irons, each other, and two THF ligands. Overall the structure of **1** is quite similar to that of $[(\text{py})_2\text{FeFe(CO)}_4]_2$,[9] in which a similar distortion of the carbonyl groups perpendicular to the Fe_4 plane was also observed.

The primary topic of interest for these compounds is the metal−metal bonding. In a purely ionic model the molecule would be considered to be made up of two Mn(THF)_2^{2+} cations and two Fe(CO)_4^{2-} anions held together by electrostatic attraction. This situation would manifest itself by low C−O stretching frequencies in the infrared spectrum and a large magnetic susceptibility indicative of the ten unpaired electrons (five per manganese) expected for two Mn^{2+} ions in pseudotetrahedral fields. In a covalent scheme the Effective Atomic Number Rule suggests that each iron atom forms single bonds to both manganese atoms in order to achieve an 18-electron configuration. There are then two possibilities, depending upon whether or not there is any direct bonding between the manganese atoms. The value of 5.0(1) μ_B for the effective magnetic moment (μ_eff) of **1** is in excellent agreement with the theoretical spin-only value of 4.9 μ_B for four unpaired electrons per molecule. Assuming that the iron atoms satisfy the EAN rule, and taking into account the crystallographic symmetry of the molecule, this result leads to the rather interesting conclusion that each manganese atom has two unpaired electrons and uses an odd number of electrons to interact with the other metals. This is consistent with a covalent model in which each manganese retains four of its valence electrons, two of which are unpaired, and uses the remaining three electrons to form two Mn−Fe bonds and an Mn−Mn bond. The manganese atoms can then be considered to have either 14 or 18 electrons in their valence shells, depending upon whether the THF ligands are counted as 2- or 4-electron donors. Examination of the carbonyl stretching region of the infrared spectrum of **1** in solution indicates that there is substantial polar character to the Mn−Fe interaction. The relatively low frequency absorptions of 1964 (s), 1898 (s), and 1869 (s) cm^{-1} are in the region associated with electron-rich anionic species such as $\text{Na}_2\text{Fe}_2(\text{CO})_8$ (ν_CO, *N*,*N*-dimethylformamide solution: 1916 (m), 1866 (s), 1842 (w) cm^{-1}),[17] and they are approximately midway between $\text{Na}_2\text{Fe(CO)}_4$ (ν_CO, *N*,*N*-dimethylformamide solution: 1730 cm^{-1})[17] and a neutral metal carbonyl such as $\text{FeMn}_2(\text{CO})_{14}$ (ν_CO, hexane solution: 2067 (s), 2019 (s), 1987 (w) cm^{-1}).[12]

In summary, $\{\mu\text{-Mn(THF)}_2\}_2\text{Fe}_2(\text{CO})_8$ is an intriguing example of a paramagnetic "xenophilic" metal cluster that contains metal carbonyl fragments covalently bonded to metals that are attached solely to donor ligands that have no π-acid capabilities. Infrared spectra suggest that the electronic charges on the metal atoms are intermediate between zero-valent metals and a purely ionic model containing Mn(THF)_2^{2+} cations and Fe(CO)_4^{2-} anions.

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Supporting Information Available: Tables giving full crystallographic data, atomic positional parameters, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates for compound **1**, as well as *U*(eq) values for the metal atoms in the alternative least-squares refinements (6 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.

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